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## REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1906.

Received November 18, 1905.

DURING the year 1905 there has been unusual activity in the determination of atomic weights, and some of the work done relates to the most fundamental values. The entire system of atomic weights is thus affected, more or less profoundly; and a general revision of the table would seem to be needed within the near future. Neglecting minor investigations, the more important determinations published since our last report are briefly as follows:

*Cadmium.*—Atomic weight determined by Baxter and Hines,[1] by analysis of the chloride. Three measurements of the ratio $CdCl_2 : 2AgCl$ gave in mean Cd = 112.476. Six measurements of the ratio $CdCl_2 : 2Ag$ gave in mean Cd = 112.462. General mean of both series, 112.469, when Ag = 107.93 and Cl = 35.473. As additional determinations are promised, based upon a study of cadmium bromide, a change in the atomic weight of cadmium as given in our table may properly be deferred.

*Carbon.*—From the ratios published in 1904, relative to the basic acetate and acetylacetonate of glucinum, Parsons[2] has computed the atomic weight of carbon. The values obtained by treating the two ratios algebraically are Gl = 9.112 and C = 12.007. As the latter figure is quite independent of all previous determinations it has distinct corroborative significance.

[1] This Journal, 27, 222.

[2] Id. 27, 1204; Z. anorg. Chem. 46, 215.

*Chlorine and Sodium.*—In a very elaborate investigation upon the atomic weights of chlorine and sodium, Richards and Wells[1] have shown that the data furnished by Stas are affected by appreciable errors. Ten syntheses of silver chloride gave, in mean, Cl = 35.473 when Ag = 107.93. From ten measurements of the ratio Ag : NaCl, and ten of the ratio AgCl : NaCl, with the foregoing values for silver and chlorine, Na = 23.008. The Stas values are Cl = 35.455 and Na = 23.048.

The results just cited are obviously indirect, for they depend upon the atomic weight of silver. The experiments published by Dixon and Edgar[2] are therefore of peculiar interest, for they involve the intervention of no intermediate quantities between the atomic weights of chlorine and hydrogen. Hydrochloric acid was directly synthetized from weighed amounts of hydrogen and chlorine, and nine concordant determinations gave, in mean, Cl = 35.195 ± 0.0019, referred to the hydrogen standard. With O = 16, Cl becomes 35.463, a value nearly midway between that found by Stas and the new figure given by Richards and Wells. Considering the difficulties of the work, the agreement between this and the previous investigations is as close as could be reasonably expected.

*Gadolinium.*—Urbain,[3] from ten analyses of the octohydrated sulphate, finds Gd = 157.23, when H = 1.007 and S = 32.06. This value is more than a unit higher than that given in the table, and is probably more trustworthy.[4]

*Iodine.*—Baxter has continued his research of 1904 upon the atomic weight of iodine, and has published a second memoir upon this subject.[5] First, from eight conversions of silver iodide into bromide, by heating in bromine, he found I = 126.985. Two series of measurements, of five experiments in each, of the ratio AgI to AgCl, gave respectively 126.982 and 126.984. Eight determinations of the direct ratio between silver and iodine, weighed separately, gave in mean 126.987. Five determinations of the ratio I : AgI gave 126.983, and four of the ratio Ag : AgI

[1] Published by the Carnegie Institution of Washington, 70 pp., April, 1905. See also this Journal, **27**, 459.

[2] Chem. News, **91**, 263. Memoir read before the Royal Society.

[3] C. R. **140**, 583.

[4] See Eberhard, Z. anorg. Chem. **45**, 374, "On the Spectroscopic Purity of the Rare Earth Oxides Studied by Urbain and Others."

[5] This Journal, **27**, 876.

gave 126.989. The average of all six series is I = 126.985, when Ag = 107.93, Cl = 35.473, and Br = 79.955. The last of these antecedent values was checked by a direct comparison of AgBr with AgCl, and the mean of six experiments gave Br = 79.953. The value previously found by Baxter was 126.975 for iodine, and the difference is partly due to his use, in the later investigation, of the new figure obtained for chlorine by Richards and Wells. The iodine work, therefore, is confirmatory of the latter.

*Nitrogen.*—R. W. Gray, in a preliminary notice,[1] gives the results of his experiments upon nitric oxide. Ten determinations of the density of the gas, corrected by the formula of D. Berthelot, give a molecular weight of 30.005, whence N = 14.005. Six analyses of nitric oxide, effected by burning finely divided nickel in it, gave N = 14.006. The investigation was to be continued farther.

Guye, in an interesting lecture before the Chemical Society of Paris,[2] has given a complete summary of the researches relative to this atomic weight, which have been conducted by him and his associates at Geneva. He also discusses, somewhat fully, all previous determinations of the constant, and concludes, mainly from the physical evidence, that the atomic weight of nitrogen is not far from 14.01, and that the Stas value, 14.04, is no longer tenable. Going still farther, he reverses the ordinary gravimetric ratios from which the accepted atomic weight of nitrogen was derived, and applying to them the new value for N, he deduces the atomic weight of silver. The latter is thus reduced from 107.93 to below 107.89, ranging even as low as 107.871. For these low values Guye cites much confirmatory evidence, which is not to be lightly disregarded. To this point we shall recur later.

*Potassium.*—Atomic weight redetermined by Archibald,[3] through analyses of the chloride. Four measurements of the ratio AgCl : KCl gave K = 39.139, and four of the ratio Ag : KCl gave 39.140, when Ag = 107.93 and Cl = 35.455. If Cl = 35.473, then K becomes 39.122.

*Silicon.*—W. Becker and J. Meyer[4] have determined the atomic

[1] Pr. Chem. Soc. **21**, 156.

[2] Bull. soc. chim., August 5, 1905, with independent pagination. Compare Richards: Proc. Amer. Phil. Soc. **43**, 116 (1904).

[3] Trans. Roy. Soc. Canada [2] **10** (Section III), 47.

[4] Z. anorg. Chem. **43**, 251; **46**, 45.

weight of silicon by conversion of the chloride into the oxide. Eight determinations were made, and in sum, 46.82400 grams of $SiCl_4$ gave 16.58236 of $SiO_2$. Hence, with Cl = 35.45, Si = 28.207. With the Richards-Wells value for chlorine, 35.473, Si becomes 28.257. Additional determinations, by a different method are promised. This paper is preceded by an essay by Meyer on the calculation of atomic weights,[1] which deserves careful consideration.

*Strontium.*—From four measurements of the ratio $2Ag : SrCl_2$, Richards[2] finds Sr = 87.661, when Ag = 107.93 and Cl = 35.473. This confirms the earlier value, derived by Richards from experiments upon strontium bromide.

*Tellurium.*—Gallo[3] has determined electrolytically the ratios between silver and tellurium. From twelve experiments, in mean, Te = 127.61, when Ag = 107.93. Incidentally to this work, as a check upon the method employed, four comparisons between silver and copper were made. In mean, Cu = 63.58.

*Thorium.*—R. J. Meyer and Gumperz[4] have attempted to separate ordinary thorium into fractions of different atomic weights, and have failed to verify the observations of Baskerville. The fractions obtained by various processes gave atomic weights varying from 232.2 to 232.7, values which are essentially identical with that given in the table.

From the foregoing summary of results it becomes evident that a far-reaching series of changes will soon be needed in our system of atomic weights. A change in chlorine or nitrogen implies many other changes in the table, and if the accepted value for silver should be modified, the alterations would be most sweeping. The atomic weights of silver, chlorine and bromine enter into the calculation of nearly all other atomic weights, and form, so to speak, the platform upon which the entire structure stands.

The changes, however, which are suggested at present are not final. Work is in progress in several laboratories, which may confirm or modify many of the accepted values, and until that work is finished, at least so far as the fundamental data are con-

[1] Z. anorg. Chem. p. 242.

[2] Pr. Am. Acad. 40, 603.

[3] Atti Accad. Lincei [5] 14, 23 and 104.

[4] Ber. 38, 817.

cerned, it is wisest for us to suspend judgment and await developments. Were we to reconstruct the table of atomic weights on the basis of the evidence now before us, we should do it imperfectly, and a new revision would be demanded next year or the year after. Confusion would inevitably follow. Fortunately, the matter is not urgent, for the corrections which now seem desirable are not large, and the existing figures are accurate enough for all ordinary purposes. We therefore recommend that the table for 1905 be continued in use without change during 1906, even though some modifications are theoretically desirable. A year hence we shall be in a better position for a critical adjustment of the data, and no harm can follow from the delay. In accordance with the expressed wish of a majority of the larger committee, we also recommend that the table based upon the oxygen standard be made official. So far as this committee is concerned, the private opinions of its members will be subordinated to the desires of the majority, and the table referred to hydrogen will no longer appear as a part of its report.

For the present, a few suggestions which follow from an examination of the lecture by Guye may not be inacceptable. Rayleigh, Leduc, Guye, Gray and others, from their studies of nitrogen and its oxides, have accumulated a mass of strong evidence in favor of a lower value for nitrogen. The data furnished by Stas, on the other hand, point to the higher value which has heretofore been generally adopted. Can we abandon the one in favor of the other, and accept the new figure without reserve?

On behalf of the new figure for nitrogen we must admit that the determinations are remarkably concordant, and that they rest upon a direct comparison of the element with oxygen. The Stas values, with their confirmations by other chemists, are also very concordant, but they are indirect. They all rest primarily upon the atomic weights of silver, chlorine and bromine, and these were connected with oxygen through experiments upon chlorates and bromates. Our whole system of atomic weights, with only a few exceptions, is based to-day upon the analyses of several oxy-halogen salts. Their accuracy is assumed, and all anomalies which appear in determinations based upon other lines of research, are commonly ascribed to undiscovered errors.

The assumption may be sustained, but it is not yet beyond the reach of criticism.

Consider, for example, the well-known ratio $Ag : AgNO_3 = 100 : 157.479$. If $Ag = 107.93$, as determined through the analyses of chlorates and bromates, then $N = 14.037$, or 14.04 as given in our table. If, on the other hand, $N = 14.009$ as given by Guye, Ag becomes 107.881. The difference between the two values for silver evidently represents a difference in our methods of connecting the element with oxygen, the latter being taken as the standard. For each method strong arguments are possible, and for each value other corroborative testimony can be cited. Neither procedure is wholly free from objections, and the final conclusion, therefore, is one of uncertainty. We cannot safely reject either line of evidence, nor can we accept one as surely more exact than the other. Concordant values for silver can be derived from either method of discussion, as Guye has shown, and through them the entire system of atomic weights is affected.

In this condition of affairs the position of the committee can only be one of conservatism. It is better to retain the table we have until at least some of the doubts which now affect it have been eliminated. It seems to be essential that the foundations of the atomic weight table should be both broadened and strengthened, and that new lines of research connecting the fundamental values with oxygen should be investigated. Some work of this kind is already promised from the laboratory of Harvard University, to be carried out by Richards and his colleagues; but that need not exclude other activities. It is to be hoped that a number of investigators may take up the consideration of this problem, and that the methods of attack upon it shall be multiplied. The careful study of such salts as the sulphates, carbonates and nitrates might perhaps be profitable. Whether the organic salts of silver could be utilized for good atomic weight determinations is still uncertain.

(Signed)

F. W. CLARKE,
T. E. THORPE,
KARL SEUBERT,
HENRI MOISSAN,
*Committee.*

INTERNATIONAL ATOMIC WEIGHTS. 1906.

| | | | | | |
|---|---|---|---|---|---|
| Aluminum | Al | 27.1 | Neodymium | Nd | 143.6 |
| Antimony | Sb | 120.2 | Neon | Ne | 20 |
| Argon | A | 39.9 | Nickel | Ni | 58.7 |
| Arsenic | As | 75.0 | Nitrogen | N | 14.04 |
| Barium | Ba | 137.4 | Osmium | Os | 191 |
| Bismuth | Bi | 208.5 | Oxygen | O | 16.00 |
| Boron | B | 11 | Palladium | Pd | 106.5 |
| Bromine | Br | 79.96 | Phosphorus | P | 31.0 |
| Cadmium | Cd | 112.4 | Platinum | Pt | 194.8 |
| Caesium | Cs | 132.9 | Potassium | K | 39.15 |
| Calcium | Ca | 40.1 | Praseodymium | Pr | 140.5 |
| Carbon | C | 12.00 | Radium | Rd | 225 |
| Cerium | Ce | 140.25 | Rhodium | Rh | 103.0 |
| Chlorine | Cl | 35.45 | Rubidium | Rb | 85.5 |
| Chromium | Cr | 52.1 | Ruthenium | Ru | 101.7 |
| Cobalt | Co | 59.0 | Samarium | Sa | 150.3 |
| Columbium | Cb | 94 | Scandium | Sc | 44.1 |
| Copper | Cu | 63.6 | Selenium | Se | 79.2 |
| Erbium | Er | 166 | Silicon | Si | 28.4 |
| Fluorine | F | 19 | Silver | Ag | 107.93 |
| Gadolinium | Gd | 156 | Sodium | Na | 23.05 |
| Gallium | Ga | 70 | Strontium | Sr | 87.6 |
| Germanium | Ge | 72.5 | Sulphur | S | 32.06 |
| Glucinum | Gl | 9.1 | Tantalum | Ta | 183 |
| Gold | Au | 197.2 | Tellurium | Te | 127.6 |
| Helium | He | 4 | Terbium | Tb | 160 |
| Hydrogen | H | 1.008 | Thallium | Tl | 204.1 |
| Indium | In | 1.15 | Thorium | Th | 232.5 |
| Iodine | I | 126.97 | Thulium | Tm | 171 |
| Iridium | Ir | 193.0 | Tin | Sn | 119.0 |
| Iron | Fe | 55.9 | Titanium | Ti | 48.1 |
| Krypton | Kr | 81.8 | Tungsten | W | 184 |
| Lanthanum | La | 138.9 | Uranium | U | 238.5 |
| Lead | Pb | 206.9 | Vanadium | V | 51.2 |
| Lithium | Li | 7.03 | Xenon | Xe | 128 |
| Magnesium | Mg | 24.36 | Ytterbium | Yb | 173.0 |
| Manganese | Mn | 55.0 | Yttrium | Yt | 89.0 |
| Mercury | Hg | 200.0 | Zinc | Zn | 65.4 |
| Molybdenum | Mo | 96.0 | Zirconium | Zr | 90.6 |

*Note.*—Since this report was written and signed, several important memoirs upon atomic weights have appeared. Gray's complete research upon N, Amberg's work upon Pd, and Birckenbach's dissertation upon Bi are the most noteworthy of these additions to the 1905 list of determinations. F. W. C.

# CRUDE GLUTEN.

By F. A. Norton.

Received October 27, 1905.

The necessity of determining the gluten content in the valuation of wheats and flours is well recognized and among the different methods employed, the determination as crude gluten has been the one most often used. In this article will be considered the composition of crude gluten, the relation of the crude gluten content to that of total protein in wheat and flour and crude gluten in the valuation of wheats and flours, and in comparison with other methods of determining the content and quality of the gluten.

## THE COMPOSITION OF CRUDE GLUTEN.

Crude gluten, the insoluble proteids of wheat together with more or less adhering impurities from the non-proteid constituents of the wheat, is readily obtained by kneading a dough from wheat flour or meal in a stream of water until the wash-water is free from turbidity. Thorpe[1] gives the approximate composition of fresh crude gluten as consisting, besides water, of a certain amount of starch, fat, other débris and proteid substances differently named by various authors. Leach[2] states that crude gluten is a complex mixture of many bodies, containing besides gliadin and glutenin, small quantities of cellulose, mineral matter, lecithin and starch. Allen[3] gives much the same composition for crude gluten as Leach, stating that it consists of a mixture of proteids, principally gliadin and glutenin, together with small quantities of lecithin, fat, phytosterol, starch, cellulose, fibre and mineral matter. There has been much work done on the proteids of wheat with great discordance in results but the findings of the thorough investigation of wheat proteids by Osborne and Voorhees[4] are now generally accepted as correct. In this treatise they have shown very conclusively that gluten consists essentially of two proteids—gliadin,[5] soluble in 70 per cent.

[1] "Dictionary of Applied Chemistry," Vol. I, p. 33.

[2] "Food Inspection and Analysis," p. 230.

[3] "Commercial Organic Analysis," Vol. IV, p. 78.

[4] Am. Ch. J. 15, 392.

[5] Ritthausen and some continental chemists hold that there are three distinct proteids—glutin fibrin, gliadin and mucedin—soluble in 60 to 70 per cent. alcohol, but Osborne in a recent (Twenty-eighth Ann. Rep. Conn.

alcohol and glutenin, soluble in dilute potassium hydroxide solution—which exist as such in the wheat and which unite when moistened to form the gluten. The glutenin imparts solidity to the gluten by forming a nucleus to which the gliadin adheres, while the gliadin forms a sticky medium binding together the particles of the flour, thus rendering the dough tough and coherent. The authors quoted have evidently based their statement of the composition of crude gluten quite largely upon the work of Osborne and Voorhees with which it is in agreement.

Little can be found as to the amount of fibre, starch and other non-proteid substances in crude gluten. Wanklyn and Cooper,[1] however, state that crude gluten contains ash equal to 0.3 per cent. and fat equal to 1.0 per cent. of the flour. And Chamberlain,[2] on washing out the crude gluten in a slow stream of 1 per cent. sodium chloride solution from two straight durum wheat flours and one Kansas hard winter wheat flour, found an average nitrogen content of 13.19 per cent. for the glutens. This treatment, which should have removed all proteids except gliadin and glutenin, gives 75.14 per cent. (taking $N \times 5.7$) of true gluten in the crude gluten.

In order to determine more fully, the proteid and non-proteid substances present in crude gluten, the following proximate analysis was made on the crude gluten from a sample of mixed straight durum wheat flours, as milled in this laboratory. The flours, six in number, after thorough mixing were sampled and crude gluten and total nitrogen determined on the sample. Nitrogen was determined by the Gunning method and crude gluten by washing as directed by Wiley,[3] the gluten being dried to constant weight at 100°. Also a larger amount of crude gluten was prepared by operating on 100 grams of flour. The resulting crude gluten, after being partially dried at 100°, was ground in a mortar until it would pass a 0.5 mm. sieve and then dried until it ceased to lose weight at 100°, when it was placed in weighing-bottles and kept over sulphuric acid until sampled, for analysis. Determinations of ash, ether extract, fibre, carbohydrates other than fibre and protein were then made in duplicate on the sample,

Agr. Expt. Sta. 1904, p. 457) reinvestigation of the alcohol-soluble proteid of wheat finds the results of the former work fully confirmed.

[1] "Bread Analysis," p. 43.

[2] Bull. No. 81, p. 121, Bureau of Chem., U. S. Dept. of Agr.

[3] "Principles and Practice of Agricultural Analysis," Vol. III, p. 435.

according to the methods of the Association of Official Agricultural Chemists.[1] The starch and carbohydrates other than fibre were determined by the acid hydrolysis with determination of the resulting glucose by the Defren-O'Sullivan Method.[2] The factor 0.9 was used for the conversion of glucose to starch and the carbohydrates all returned as starch.[3] The results which follow are referred to both the crude gluten and to the flour.

| | Per cent. in crude gluten. | Per cent. recovered in crude gluten from flour. |
|---|---|---|
| Total protein (N × 5.7) | 80.91 | 13.39 |
| Ether extract | 4.20 | 0.69 |
| Fiber | 2.02 | 0.34 |
| Ash | 2.48 | 0.41 |
| Carbohydrates other than fiber | 9.44 | 1.56 |
| Total | 99.05 | 16.39 |
| Crude gluten in flour | | 16.55 |
| Total protein in flour (N × 5.7) | | 15.25 |

*Proteids in Crude Gluten.*—As it was desired to ascertain the character of the proteid contents of the crude gluten, crude gluten was obtained in duplicate, as above on two 5-gram portions of the flour and subjected to the following determinations. After completing the washing of the crude gluten, the samples were finely divided, placed in flasks and extracted with successive portions of 70 per cent. alcohol for twenty-four hours, 250 cc. of alcohol being used for each sample. The alcohol extracts were transferred to Kjeldahl digestion flasks and after distilling off the alcohol, nitrogen was determined by the Gunning process. The gluten residues were then extracted with successive portions of 10 per cent. sodium chloride solution for six hours, 250 cc. of solution being used for each sample and nitrogen determined on the extract after concentration with a little sulphuric acid. The gluten residues were then extracted with 250 cc. of 0.2 per cent. potassium hydroxide solution for six hours. Practically all the residue went into solution but a small amount remained,

[1] Bull. No. 46, Bureau of Chem., U. S. Dept. of Agr.

[2] This Journal, **18**, 749.

[3] Osborne has shown (This Journal, **25**, 474) that while a carbohydrate group is present in the protein molecule of some proteids, the amount present is extremely small, so that the method employed should give closely the non-fibre carbohydrates retained in the crude gluten. Besides the starch which could be identified microscopically in the crude gluten the hydrolysis would probably remove some pentosans and hemi-cellulose.

which appeared to be largely fibre. After filtering off and washing the residue, nitrogen was determined in the extract as with the sodium chloride extract. Results follow expressed on the flour:

| | Nitrogen in gluten from 5 grams of flour. Grams. | Per cent. of proteid (N × 5.7) recovered in the gluten from the flour. |
|---|---|---|
| Gliadin or 70 per cent. alcohol extract | 0.0564 | 6.42 |
| Glutenin or 0.2 per cent. KOH extract | 0.0505 | 5.76 |
| Globulin or 10 per cent. NaCl extract | 0.0055 | 1.11 |
| Total proteids recovered | | 13.29 |
| Total protein recovered in gluten from flour | | 13.39 |

This gives practically the same amount of protein recovered in the several extracts as by direct determination of total protein on the dry crude gluten and together with the non-proteid constituents would give the following proximate composition for the crude gluten.

| | Per cent. |
|---|---|
| Fats or ether extract | 4.20 |
| Carbohydrates other than fiber | 9.44 |
| Fiber | 2.02 |
| Ash | 2.48 |
| Gliadin | 39.09 |
| Glutenin | 35.07 |
| NaCl soluble protein | 6.75 |
| Total | 99.05 |

This gives 74.16 of gliadin and glutenin or true gluten in the crude gluten and compares very closely with Chamberlain's figures, which indicate 75.14 per cent. proteid in the crude gluten, all of which should have been true gluten. Determinations of protein on the dry crude gluten from a patent spring wheat flour, a patent durum wheat flour, a whole durum wheat meal together with the above sample gave the following results:

| | Per cent. protein (N × 5.7) in crude gluten. |
|---|---|
| Straight durum wheat flour | 80.91 |
| Patent durum wheat flour | 77.86 |
| Whole durum wheat meal | 77.52 |
| Patent spring wheat flour | 82.74 |

These show quite close agreement in the protein content and it is probable that the glutens would correspond quite closely in other respects. This would indicate that crude gluten con-

tains approximately 75 per cent. of true gluten, together with variable amounts of fat, carbohydrates, mineral matter and non-gluten proteid matter.

RELATION OF CRUDE GLUTEN TO TOTAL PROTEIN, N×5.7.

There is quite a close agreement between the crude or dry gluten and the total proteid (N×5.7) content of flour. R. Heinrich[1] states that the gluten content of wheat generally but not always rises and falls with the nitrogen content. In "Cereals and Cereal Products"[2] the authors, in discussing dry gluten, state that in general there is a common agreement in the flours analyzed, between the total percentage of dry gluten and of total proteid matter; that those flours which show a high content of total proteid matter also show a high content of dry gluten. The Columbus Laboratories in their report[3] to the Tennessee Experiment Station on the "Relative Values of Varieties of Winter Wheat for the Production of Flour and Bread" have taken N×5.7 as gluten, stating: "This was found to be more constant and reliable for work of this character than the determination of crude gluten by hand washing. In general the amounts of gluten in white flours as determined by the two methods are found to agree closely."

A great many dry gluten determinations made by the writer, in a general way, confirm the work of those quoted. However, there is a variation of from about 2 per cent. less dry gluten than protein, in some cases, with whole wheat meal to about 4 per cent. more dry gluten than protein with some straight durum wheat flours. In general, a straight or baker's grade flour gives a higher average crude gluten content in relation to the protein content than a patent flour, while a patent flour in turn gives a higher crude gluten content in relation to the protein content than a whole wheat meal.

The following determinations of dry or crude gluten collated from the results of a number of workers give the general relation between crude gluten and total protein and show that only the crude gluten of patent flours approximates very closely to the total protein content, while that of straight or baker's grade

[1] Zweiter Ber. landw. Ver. Stat. Rostock, 1894, pp. 213–223.
[2] Bull. No. 13, Part 9, p. 1259, Bureau of Chem., U. S. Dept. of Agr.
[2] Bull. of Tenn. Agr. Expt. Sta., Vol. XVI, No. 4, p. 57.

CRUDE GLUTEN.

| Flour. | No. of determinations. | Protein N × 5.7. | Dry gluten. | Difference. | By whom made. |
|---|---|---|---|---|---|
| Straight spring wheat, without low grade | 10 | 11.06 | 12.68 | +1.62 | Central Expt. Farm, Canada.[1] |
| Patent durum wheat | 10 | 12.61 | 14.13 | +1.52 | Chamberlain, Bureau of Plant Ind.[2] |
| Patent northwest spring wheat | 6 | 13.01 | 13.53 | +0.52 | " " " " " |
| Patent Kansas hard winter wheat | 1 | 12.85 | 12.64 | —0.21 | " " " " " |
| Straight Kansas hard winter wheat | 3 | 14.69 | 15.92 | +1.23 | " " " " " |
| Straight northwest spring wheat | 3 | 13.39 | 15.15 | +1.76 | " " " " " |
| Straight durum wheat | 3 | 15.65 | 17.96 | +2.31 | " " " " " |
| Whole wheat meal, all kinds | 228 | 11.13 | 10.22 | —0.91 | T. C. Trescot, Bureau of Chemistry.[3] |
| Whole wheat meal | 6 | 13.04 | 11.72 | —1.32 | Maine Expt. Station.[4] |
| Patent, spring and winter | 4 | 11.96 | 11.85 | —0.11 | Minn. Expt. Station.[5] |
| Patent | 40 | 9.62 | 9.99 | +0.37 | Bureau of Chemistry.[6] |
| Common market | 19 | 9.28 | 9.21 | —0.07 | " " " |
| Baker's grade | 14 | 11.20 | 13.07 | +1.87 | " " " |
| Straight durum, low grade included | 113 | 14.37 | 16.59 | +2.22 | Norton, South Dakota Expt. Station.[7] |
| Straight spring wheat, low grade included | 5 | 12.66 | 14.82 | +2.16 | " " " " " |
| Patent durum | 1 | 10.03 | 10.91 | +0.88 | " " " " " |
| Patent spring wheat | 1 | 10.64 | 10.35 | —0.29 | " " " " " |
| Whole durum wheat meal | 1 | 14.24 | 12.94 | —1.30 | " " " " " |

[1] "Milling and Chemical Value of the Grades of Wheat," Bull. 50, Part II.

[2] "Commercial Status of Durum Wheat," Bull. 70, Bur. of Plant Ind., Dept. of Agr.

[3] "Analyses of Cereals Collected at the World's Columbian Exposition," Bull. 45, Bureau of Chem., U. S. Dept. of Agr.

[4] "Wheats and Flours of Aroostook County," Bull. 97, Maine Expt. Sta.

[5] "Wheat and Flour Investigations," Bull. 85, Minn. Expt. Sta.

[6] "Cereals and Cereal Products," Bull. 13, Part 9.

[7] "Macaroni Wheat," Bulls. 82 and 92, So. Dak. Expt. Sta.

flour and whole wheat meal often varies several per cent. from the total protein.

In order to account for the variation in the relation of the crude gluten content to that of total protein with the different flours we will need to consider the character both of the proteids and of the non-proteid constituents. The only non-proteid which might be very largely responsible for this variation is the fibre. The writer has found the crude gluten to be very tenacious in retaining the fibre and in the analysis of crude gluten given above it is seen that the fibre recovered in the crude gluten is equal to the average fibre content for a straight grade flour. This has also been the experience of Lindet and Amman who state[1] in a discussion of the "Influence of Some Constituents of Whole Meal Flour on the Extraction of Gluten" that the gluten extracted from flour containing a small amount of bran is usually found to contain less nitrogen than is present in ordinary gluten and account for it by the fact that the bran is separated from the flour along with the gluten. As regards the fibre content, we find average amounts for the different grades of flour and whole wheat as follows:

| | Number of analyses. | Per cent. fibre. |
|---|---|---|
| Patent wheat flours | 40 | 0.21[2] |
| Baker's and family grade flours | 14 | 0.22[2] |
| Straight flours | 10 | 0.34[3] |
| Whole wheat | 228 | 2.35[4] |

It is probable that the variation between the crude gluten and protein contents is due more largely to the character of the proteids. Osborne and Voorhees[5] give the proteids of the wheat kernel approximately as follows:

| | Per cent. |
|---|---|
| Globulin | 0.6–0.7 |
| Albumin | 0.3–0.4 |
| Proteose | 0.3 |
| Gliadin | 4.25 |
| Glutenin | 4.0–4.5 |

This would give of the total proteids about 86 or 87 per cent.

[1] C. R. 141, 56–58 (1905).

[2] Bull. No. 13, Part 9, Bureau of Chem., U. S. Dept. of Agr.

[3] Bull. No. 50, Part II, Central Expt. Farm, Canada.

[4] Bull. No. 45, Bureau of Chem., U. S. Dept. of Agr.

[5] Am. Ch. J. 15, 468.

of gliadin and glutenin or true gluten. Snyder[1] has shown that the germ, bran and shorts of wheat and low-grade flour contain from two to four times more water and salt-soluble proteids than patent flours and states: "The process of milling results partly in a mechanical separation of the various proteids, the non-gluten proteids being recovered mainly in the by-products while the gluten proteids are recovered mainly in the flour. In the wheat, from 80 to 85 per cent. of the total nitrogen is in the form of gluten while in the flour there is from 86 to 89 per cent. in this form."

Of the wheat proteids, the gliadin and glutenin unite to form the gluten and should be recovered in the crude gluten. The proteose and albumen are water-soluble and would be lost in the washing. The globulin is only soluble in salt solutions and would probably be very incompletely removed, as its separation would be mechanical, as with starch and fibre. In addition to these proteids, the nitrogen of wheat consists also of amide nitrogen. Investigators[2] have isolated the amide compounds principally from the germ of the wheat and determinations by different workers indicate that the offal products in the milling of the wheat contain most of the amide bodies, patent flour being practically free. The amides are readily water-soluble and would be lost in washing out the gluten. In order to determine more fully the relative amounts of the proteid and amide bodies in whole wheat and the different flours, the following determinations were made on the same samples as referred to in the fore-part of this article. The methods employed were those outlined by Snyder[3] and based upon the work of Osborne and Voorhees. Results follow together with determinations by Snyder on two patent flours and one baker's grade flour.

| | Total nitrogen. Per cent. | Water soluble nitrogen. Per cent. | NaCl soluble nitrogen. Per cent. |
|---|---|---|---|
| Straight durum wheat flour | 2.68 | 0.46 | 0.33 |
| Patent spring wheat flour | 1.87 | 0.38 | 0.15 |
| Whole durum wheat meal | 2.50 | 0.49 | 0.34 |
| Average of two patent spring wheat flours | 2.24 | 0.42 | 0.20 |
| Baker's grade flour[4] | 3.28 | 0.38 | 0.30 |

[1] Ann. Rep. Minn. Expt. Sta., 1899, p. 529.

[2] Bull. No. 13, Part 9, p. 1207.

[3] Ann. Rep. Minn. Expt. Sta., 1899, p. 524: also Bull. 81, p. 103, Bureau of Chem., U. S. Dept. of Agr.

[4] Ann. Rep. Minn. Expt. Sta., 1899, p. 524.

The water-soluble gliadin nitrogen and the amide nitrogen were then determined and the non-gluten nitrogen calculated by subtracting the water-soluble gliadin nitrogen from the water-soluble nitrogen and adding the sodium chloride-soluble nitrogen to the latter.

| | Amide nitrogen. Per cent. | Water-soluble gliadin nitrogen. Per cent. | Nitrogen of albumen and proteose. Per cent. | Non-gluten nitrogen of total nitrogen. Per cent. |
|---|---|---|---|---|
| Straight durum wheat flour..... | 0.04 | 0.29 | 0.13 | 18.65 |
| Patent spring wheat flour..... | 0.02 | 0.25 | 0.11 | 14.97 |
| Whole durum wheat meal ..... | 0.09 | 0.24 | 0.16 | 23.60 |
| Patent spring wheat flours— average of two..... | 0.016 | 0.34 | 0.08 | 13.80 |
| Baker's grade flour..... | 0.024 | 0.29 | 0.09 | 12.93 |

From the above we can see that the best flours contain more true gluten but considerably less sodium chloride-soluble proteid which might be retained in the washing out of the crude gluten. Also that there would be more loss from amide nitrogen and water-soluble proteids with the whole wheat and low-grade flours than with patent flours.

Since the washing out of the crude gluten is a comparatively rough process, we have now to consider what loss of true gluten might take place during the operation. Osborne and Voorhees,[1] in their work on wheat proteids, report that they obtained the same amount of gliadin by direct extraction of the whole wheat meal with 70 per cent. alcohol as by the extraction of the crude gluten from an equal amount of the meal. Snyder,[2] however, found that direct extraction of flour with alcohol for the determination of gliadin gave better results and offered fewer difficulties than the extraction of the gluten mass from a like quantity of flour. In the flours previously described we have the following percentages of the total protein of the flour recovered in the crude gluten. Determinations on a spring wheat and a winter wheat meal by Osborne and Voorhees are included.

[1] Am. Ch. J. 15, 440, 441.

[2] Ann. Rep. Minn. Expt. Sta., 1899, p. 531.

| | Protein ($N \times 5.7$) in flour. Per cent. | Dry gluten in flour. Per cent. | Protein in crude gluten. Per cent. | Total protein of flour recovered in crude gluten. Per cent. |
|---|---|---|---|---|
| Straight durum wheat flour..... | 15.25 | 16.55 | 80.91 | 87.80 |
| Patent spring wheat flour..... | 10.64 | 10.35 | 82.74 | 80.49 |
| Patent durum wheat flour..... | 10.03 | 10.91 | 77.86 | 84.69 |
| Whole durum wheat meal ..... | 14.24 | 12.94 | 77.52 | 70.44 |
| Whole spring wheat meal[1]..... | 11.93 | 12.69 | 68.46 | 72.82 |
| Whole winter wheat meal[1]. .... | 10.96 | 11.86 | 68.40 | 74.02 |

The above table shows, as the character of the proteids indicated, that more of the total nitrogen is recovered in the crude gluten of flours than in the crude gluten of whole wheat meals. In regard to the relation of total protein recovered to the true gluten content of the several samples we also find variations. In the case of the straight durum wheat flour, we have, by subtracting the non-gluten nitrogen, 81.35 per cent. of true gluten while 87.80 per cent. of the total protein of the flour was recovered in the crude gluten. In the determinations of the proteids in the crude gluten from this flour as given above we found the following percentages for the proteid bodies present.

| | Total proteids in crude gluten. Per cent. |
|---|---|
| Gliadin..... | 48.31 |
| Glutenin..... | 43.35 |
| NaCl soluble in proteid..... | 8.34 |

This would give 91.66 per cent. of the proteids of the crude gluten as true gluten and 80.47 per cent. of true gluten recovered from the flour as against the true gluten content of 81.35 per cent., which would indicate some loss of true gluten. With the patent flours and whole wheat meal there was less total protein recovered from the flour than the true gluten contents so there must have been considerable loss of true gluten. The two determinations by Osborne and Voorhees show about the same amount of proteids recovered in the crude gluten as in the determination by the writer on whole wheat meal. Osborne and Voorhees[1] give the following proteid composition for the two wheats.

[1] Am. Ch. J. 15, 461.

| | Spring wheat. | | Winter wheat. | |
|---|---|---|---|---|
| | Nitrogen. | Proteid. | Nitrogen. | Proteid. |
| Glutenin | 0.8246 × 5.68 | = 4.683 | 0.7346 × 5.68 | = 4.173 |
| Gliadin | 0.6977 × 5.68 | = 3.963 | 0.6884 × 5.68 | = 3.910 |
| Globulin | 0.1148 | = 0.624 | 0.1148 | = 0.625 |
| Coagulum | 0.0453 | = 0.269 | 0.0379 | = 0.223 |
| Albumin | 0.0657 | = 0.391 | 0.0603 | = 0.359 |
| Proteose | 0.0341 | = 0.213 | 0.0791 | = 0.432 |
| From $H_2O$ washings of gluten | 0.2239 × 5.68 | = 1.272 | 0.1552 × 5.68 | = 0.881 |
| Total | 2.0050 | 11.415 | 1.8703 | 10.603 |
| Flour | 2.10 × 5.68 | = 11.93 | 1.94 × 5.68 | = 10.96 |

This gives for the two wheats the following percentages of gluten and non-gluten nitrogen in the total nitrogen.

| | Spring wheat. | Winter wheat. |
|---|---|---|
| True gluten | 72.64 | 73.35 |
| Non-gluten | 12.55 | 15.06 |
| $H_2O$ washings | 10.66 | 8.00 |
| Difference between total and proteid nitrogen, probably amide nitrogen | 4.15 | 3.39 |

As Osborne and Voorhees determined the gliadin and glutenin in the above analysis on the crude gluten obtained by washing a definite amount of the whole wheat meal, any loss of true gluten would be found in the aqueous washings, and it is probable that the true gluten content of the two wheats was somewhat higher than the figures for gliadin and glutenin would indicate. Nevertheless, their figures as to proteids recovered in the crude gluten agree in general with those of the writer.

As to the loss of true gluten, this seems to be greatest in the patent flours and whole wheat meals and must be due to the impairment of the agglutinating power. Macaroni manufacturers object to the flour or semolina for the manufacture of macaroni being finely ground, as in so doing it loses what is called its "force"[1] *i. e.*, its agglutinating power is impaired and this may account for the greater loss of true gluten in the patent flour. In patent flours the smaller sodium chloride-soluble proteid content would also lower the amount of proteids recovered in the crude gluten from the flour. With the whole wheat meal, the large fibre content and perhaps some other

[1] "Manufacture of Macaroni and Semolina," Bull. 20, p. 25, Bureau of Plant Industry, U. S. Dept. of Agr.

factors would effect the agglutinating power of the gluten. Lindet and Amman[1] state that while the gluten of white flour is readily separated by washing and kneading the cake of dough under a stream of water, in the case of whole meal flours or mixtures of the same with white flour a coherent mass of gluten cannot be obtained and ascribe this lack of agglutinating power to the greater acidity of the whole meal flour, to the presence of a mucilaginous substance and greater glutenin content with smaller gluten content, and to the effect of the bran in preventing agglutination. The writer has had no great difficulty in securing good duplicate results in determining the crude gluten on whole wheat meal. Other workers in this country have made a great many determinations of crude gluten on whole wheats, yet it is quite certain that the bran, at least, more or less affects the agglutinating power of the gluten of whole wheat meal.

From the above discussion it will be seen that all of the nitrogen of the flour is not recovered in the crude gluten and thus the relation of dry gluten to total protein in a flour is the balance between the loss of proteid and amide bodies and gain by retention of fibre, starch and other non-proteid matters. The crude gluten from whole wheat flours is the least pure, more non-proteid matter being retained but the greater loss of nitrogenous bodies due to the larger content in the flour of amide compounds and non-gluten proteids, together with greater loss of true gluten, brings the crude gluten content below that of the total protein content. In patent flours there are less non-proteid substances retained in the crude gluten and probably also less of the sodium chloride-soluble proteid which, together with some loss of true gluten, brings the total proteid and crude gluten content nearly the same. In straight and low-grade flours a somewhat larger content of fibre and sodium chloride-soluble proteid together with probably less loss of true gluten especially in coarser flours brings the crude gluten content considerably above that of the total protein.

### GLUTEN IN THE VALUATION OF WHEATS AND FLOURS.

Most investigators of wheat and flour determine the crude gluten as a means of ascertaining the bread value of the flour. Some workers determine only the dry crude gluten, others only

[1] C. R. 141, 56–58 (1905).

the moist or wet gluten, while others determine both and express the relation of the two as water capacity.

The moist gluten is usually determined by making 10 grams of flour into a stiff dough, and after allowing it to stand for an hour for the gluten to form, the dough is washed in a stream of cold water until the wash-water is free from turbidity. After standing another hour, the gluten is removed from the dish and the adhering water removed as completely as possible by kneading the gluten mass between the fingers or the moist gluten is permitted to air-dry for a time, when it is weighed and the weight recorded as moist gluten. Dry gluten is determined by drying the moist gluten to constant weight at 100°. The water content or capacity of the gluten is expressed either as the ratio of dry to moist gluten or as the water held by each gram of dry gluten. There are then really two determinations, that of crude gluten either dry or moist and water capacity of the gluten.

*The Water Capacity of Glutens.*—The reason given for this determination is that a well hydrated gluten lends itself more readily to the fabrication of a loaf of good porosity, sponginess and weight, *i. e.*, a high water content tends to a greater bread yield. There is considerable variation in the water content of glutens as may be seen from the following determinations collated from the reports of a number of workers.[1]

| | No. of determinations. | Water held by each gram dry gluten. Grams. |
|---|---|---|
| Patent flours | 40 | 1.60[2] |
| Baker's grade flours | 14 | 1.65[2] |
| Straight spring wheat flours with low-grade flour discarded | 10 | 1.86[3] |
| Straight spring wheat flours with low-grade flour included | 5 | 2.10[4] |
| Straight durum wheat flours | 113 | 1.96[4] |
| Patent durum wheat flours | 3 | 1.85[4] |

In these determinations we see a general tendency for the better flours to have a low water content. However, results seem to be far from consistent, for Shutt[5] reports practically

[1] The references to the literature containing the above determinations may be found in connection with the determinations of crude gluten cited.

[2] Made by Bureau of Chemistry.

[3] Made by Central Experiment Farm, Canada.

[4] Made by South Dakota Experiment Station.

[5] Bull. 50, Part II, p. 17, Central Experiment Station, Canada.

the same water content for the crude gluten for flours from No. 1 hard and No. 1 Northern wheats as for the flour from wheats graded "feed" and No. 5 frosted. The writer, in a great many determinations on straight durum wheat flours, has found very contradictory results, as sometimes the gluten of the best flours and sometimes that of the poorer ones gave the highest water content. In general, as seen with the patent flours, there seems to be a tendency for the best flours as regards bread purposes to have a low water content. The explanation of this would seem to lie in the higher glutenin content of the gluten of low-grade flours. H. A. Guthrie[1] states that the strength or water-absorbing capacity of a flour depends directly upon the relative proportions in which gliadin and glutenin are present in the gluten and that if the gluten content is nearly the same for two flours that will be the stronger flour which contains the larger proportion of glutenin. Fleurent[2] states that bread made with a flour whose gluten contains as little as 20 per cent. of glutenin rises well during fermentation but flattens in baking. One always uses too much water with such a flour. When the gluten approaches 34 per cent. of glutenin the dough neither rises during fermentation nor in the oven and the bread remains heavy and indigestible. The character of the dough in the latter case cited by Fluerent would indicate too large a water absorption. The experience of the writer agrees with that of those quoted. The following example from our work on durum wheat flours, while characteristic of many other samples, is especially striking. The flour had a high crude gluten content—17.45 per cent. dry gluten—with a water capacity for the gluten slightly above the average and a high water absorption capacity for the flour. The flour yielded a dough which failed to give a good sponge or to rise well during baking, and the bread was heavy, dark, or of very poor texture and the loaf was only about three-fourths the size of the usual loaf from the same amount of flour. The gliadin content of this flour was abnormally low, only 35.74 per cent. of the total protein, which would indicate a decided excess of glutenin. If a gluten has a good water capacity with proper physical qualities, it would be desirable, but there does not seem to be anything very definite about the values obtained and often a high water

[1] Agl. Gaz. N. S. Wales, 1896, No. 9, pp. 583–590.

[2] Manuel l'analyse Chimique, 1898, pp. 308–314.

content goes with excess of glutenin and poor bread-making properties, so that the determination does not seem to be of much value.

*Crude Gluten in the Valuation of Wheats and Flours.*—The crude gluten is reported sometimes as dry and sometimes as moist gluten. Unless it is desired to report the moist gluten in addition to the dry, it would seem much better to report it in the latter form as the personal equation enters largely into the determinations of moist gluten and even on duplicate samples it is difficult for the same person to get strictly concordant results. The writer, while finding it comparatively easy to get two duplicate samples of dry gluten to agree within 0.1 to 0.2 per cent., has sometimes had the same duplicates vary from 0.5 to 1.0 per cent. on the moist gluten determination.

As to the value of crude gluten as an indication of the value of a flour for bread-making purposes, there certainly is no direct relation between the amount of crude gluten and the volume and texture of the loaf. Snyder,[1] in discussing the bread-making values of roller mill products, states: "a high gluten content does not necessarily imply a large loaf or good bread-making qualities. The sample with the largest gluten content was the fourth break flour which produced a rather small loaf, and one of poor quality. A high gluten content is desirable, provided the gluten is of good quality." The following determinations by the writer on spring and durum wheat flours show how little the volume and the quality of the bread depends upon the crude gluten content of the flour. Results are averages for the flours taken.

| | Dry gluten. Per cent. | Volume of loaf. cc. | Weight of loaf. Grams. | Rank as to texture and quality. |
|---|---|---|---|---|
| Five best straight durum wheat flours... | 16.94 | 1580 | 455 | 2 |
| Five poorest straight durum wheat flours | 17.12 | 1290 | 450 | 3 |
| Five straight spring wheat flours..... | 14.82 | 1630 | 447 | 2 |
| Two patent durum wheat flours..... | 13.38 | 1650 | 430 | 1 |
| One patent spring wheat flour..... | 10.35 | 1700 | 435 | 1 |

While the crude gluten content is not a criterion of the bread-making value of the flour, yet some idea of the quality of the gluten can be obtained from the crude gluten and a general impression of the value of the flour for bread purposes can be gained. Thus if the gluten is separated with difficulty on washing and is

[1] Bull. No. 85, p. 197, Minn. Expt. Sta.

short or lacking in elasticity, a deficiency of gliadin is indicated and the flour will not make good bread. On the other hand, if the separated gluten lacks body, *i. e.*, spreads out very readily when made into a ball and is over-sticky, an excess of gliadin is indicated and the flour will be equally poor for bread purposes. Nevertheless, no very close values as to the bread-making properties of a flour can be obtained directly from the crude gluten.

The baker's sponge test[1] in connection with the determination of crude gluten gives values which are very indicative of the character of the gluten, as may be seen from determinations on the flours just cited.

| | Dry gluten. Per cent. | Average rise for 100 grams flour. cc. | Average rise for each gram dry gluten. cc. | Volume of loaf. cc. |
|---|---|---|---|---|
| Five best straight durum wheat flours | 16.94 | 670 | 39.45 | 1580 |
| Five poorest straight durum wheat flours | 17.12 | 528 | 30.84 | 1290 |
| Five straight spring wheat flours | 14.82 | 652 | 44.00 | 1630 |
| Two patent durum wheat flours | 13.38 | 650 | 48.60 | 1650 |
| One patent spring wheat flour.. | 10.35 | 720 | 69.56 | 1700 |

However, if a flour gives a good sponge test, that is, an expansion of 650 to 700 cc. for the dough from 100 grams of flour, the experience has been that it will have good bread values, no matter what the crude gluten content may be.

Determination of gliadin might be made on the crude gluten to ascertain whether gliadin and glutenin were present in proper proportions, but it would be more satisfactory to make the determinations on the flour and compare the gliadin content with that of total protein, as closer values could thus be obtained.

It would thus seem that the determination of crude gluten is of questionable value in the valuation of flours and wheats. Snyder, who has been very active in the investigation of flours and wheats, would seem to be of the same opinion. In a recent publication[2] on the testing of wheat flour for commerical purposes he states: "The determinations which have given the best satisfaction in flour testing are moisture, ash, total nitrogen, gliadin nitrogen, granulation, absorptive capacity and color." The same con-

[1] This Journal, 27, 929.

[2] Ibid. 27, 1069.

clusion has been reached by M. Aprin[1] who, after a study of the errors involved in estimating moist gluten, found the method so subject to error as to be entirely unsatisfactory, and he recommends the abandoning of the determination of moist gluten and falling back on the nitrogen content of the flour as a means of judging of its gluten content.

*Other Methods of Determining the Gluten Content of Flours.*—Among the chemical methods proposed for determining the gluten of flour is that of Fleurent[2] which has been modified by Mangent.[3] In this method the crude gluten is obtained by washing a dough in dilute sodium chloride solution. The separated gluten, after completing the washing, is finely divided and extracted with alcoholic potassium hydroxide solution and gliadin and gluten determined on the extract. The method seems somewhat tedious and results obtained by Chamberlain[4] in a study of the method would indicate that the results obtained are too high. Methods for the determination of wheat proteids, as outlined by Snyder and previously referred to in this article, give good results for the determination of gliadin and glutenin as also do the methods outlined by Chamberlain[5] and based upon the work of Osborne, Voorhees and Snyder. Teller[6] has also proposed methods which give quite concordant results, though it seems advisable always to determine soluble gliadin in the sodium chloride extract.

A more simple method recently proposed is the determination of total nitrogen and gliadin nitrogen and expression of the ratio of gliadin to total protein ($N \times 5.7$). There are not many gliadin determinations on flours recorded. Snyder,[7] however, has suggested that a flour to possess good bread-making properties should contain about 11 per cent. of total protein ($N \times 5.7$) and that 55 to 65 per cent. should be in the form of gliadin.

The experience of the writer is in accord with the above standard and these determinations, which are very accurate and at the same time comparatively simple and rapid, next to the baker's

[1] Ann. Chim. Analyt. 7, Nos. 9–10–11 (1902).
[2] Manuel l'Analyse Chimique, 1898, pp. 308–314.
[3] Rev. intern. des falsif., 1902, p. 91.
[4] Bull. 81, pp. 118–125, Bureau of Chem., U. S. Dept. of Agr.
[5] Bull. 81, p. 124, Bureau of Chem., U. S. Dept. of Agr.
[6] Ark. Expt. Sta., Bull. 42, p. 96.
[7] This Journal, 26, 266.

sponge test or actual baking tests have been found most indicative in determining the value of a flour for bread purposes.

SUMMARY.

Crude gluten consists of about 75 per cent. of true gluten—gliadin and glutenin—together with small percentages of non-gluten proteid, mineral matter, fat, starch, fibre and other non-proteid matter.

The relation of the crude gluten content to that of total protein ($N \times 5.7$) varies with the character of the flour, the crude gluten content being greater than total protein for straight and low-grade flours, nearly the same for patent flours and less for whole wheat meal.

Crude gluten is an expression, in addition to the true gluten content of a flour, of the balance between the loss of non-gluten proteids and gain from the retention of non-proteid substances. The relation of the crude gluten content to the total protein content can thus be explained by the varying composition of the different flours in respect to nitrogenous compounds and non-proteids.

Crude gluten is a very rough expression of the gluten content of a flour or wheat and the determination has but little worth in the valuation of flours.

The determination of total nitrogen and gliadin nitrogen with expression of the ratio of gliadin to total protein ($N \times 5.7$) seems to be the best simple method at hand for estimating the gluten content and ascertaining the character of the gluten in the valuation of wheats or flours.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## THE CHEMISTRY OF FLESH.

### (THIRD PAPER.)[1]

## A STUDY OF THE PHOSPHORUS CONTENT OF FLESH.

BY A. D. EMMETT AND H. S. GRINDLEY.

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IN CONNECTION with the researches upon the chemistry of flesh which are being made in this laboratory, it seemed desirable

[1] This Journal, **26**, 1086 (1904); **27**, 658 (1905).

to include a somewhat detailed study of the amounts and also of the nature of the various phosphorus compounds occurring in flesh.

Recently much work has been devoted to the study of the changes which the phosphorus compounds of seeds undergo during germination. The investigators who have been most active in this field of research are Iwanoff,[1] Zaleski,[2] Hart and Andrews,[3] Schulze and Castoro,[4] and Patten and Hart.[5]

Important investigations have also been made in determining the character of the phosphorus compounds of certain classes of animal substances. In this connection, mention should be made of the work of Katz,[6] Macleod,[7] Percival,[8] and Koch.[9]

Notwithstanding the fact that valuable information has been obtained during the last decade regarding the phosphorus compounds of certain animal substances, as yet, so far as the authors have been able to find, no systematic study has been undertaken which has for its object the determination of the quantities, the distribution and the nature of the inorganic and the organic compounds of phosphorus occurring in the different species of animals, the flesh of which is used as food for man. This paper records the results which have been obtained thus far in an investigation having in view the above object.

## PRELIMINARY STUDY OF METHODS.

The methods for the separation and estimation of the inorganic and the organic forms of phosphorus are as yet imperfect. Zaleski,[10] in studying the changes which the phosphorus compounds of seeds undergo during germination, used as a solvent a 0.2 per cent. solution of hydrochloric acid. In the extract thus obtained he determined the inorganic, the organic and the total phosphorus. Zaleski separated the soluble inorganic phosphorus from the soluble organic phosphorus by precipitating the former with the

[1] Ber. bot. Ges. **20**, 366 (1902).
[2] Ibid. **20**, 426 (1902).
[3] Am. Ch. J. **30**, 470 (1903).
[4] Z. physiol. Chem. **41**, 477 (1903).
[5] Am. Ch. J. **31**, 564 (1904).
[6] Archiv. Ges. Physiol. **63**, 1 (1896).
[7] Z. physiol. Chem. **28**, 535 (1899).
[8] C. R. **135**, 1005 (1902).
[9] Am. J. Physiol. **11**, 303 (1904).
[10] Ber. bot. Ges. **20**, 426 (1902).

regular acid ammonium molybdate solution. He apparently considered that none of the organic phosphorus compounds would be changed by the action of the free nitric acid, and consequently that only the phosphorus already oxidized would be thrown down. The organic phosphorus was obtained indirectly by subtracting from the total soluble phosphorus, the amount of inorganic phosphorus determined by direct precipitation.

Iwanoff[1] also determined the inorganic phosphorus directly by using the ordinary acid ammonium molybdate solution. He stated that the influence of the nitric acid in the precipitating reagent was insignificant and that the organic matter did not interfere with the precipitation of the phosphates.

Hart and Andrews,[2] as a result of their work, claimed that the presence of the free nitric acid in the molybdate solution causes a removal of some of the phosphorus from the organic compounds. Their results prove that such an action does take place when nucleic acid from wheat bran is treated with the acid ammonium molybdate solution. Hart and Andrews therefore modified the usual method by using a neutral solution of the molybdate and just enough of free nitric acid to cause a separation of the ammonium phosphomolybdate.

Schulze and Castoro[3] have called attention to the fact that the modified method of Hart and Andrews might be at fault in that all the inorganic phosphorus under such conditions may not be precipitated. Grete[4] found that in the presence of organic matter considerable nitric acid must be added to obtain the separation of the phosphoric acid in the form of the molybdic compound. However, Schulze and Castoro made no direct test of the Hart and Andrews method.

A detailed study of the results of the researches of the above investigators indicates that excess of free nitric acid causes the decomposition of the organic phosphorus compounds of ungerminated and of germinated seeds. This being true, the presence of a strong mineral acid like nitric may readily cause serious changes in such complex and unstable substances as those existing in the water-soluble constituents of meats. In

[1] Ber. bot. Ges. **20**, 366 (1902).
[2] Am. Ch. J. **30**, 470 (1903).
[3] Z. physiol. Chem. **41**, 477 (1903).
[4] Konig's Unter. landwirts. u. gewerb. Stoffe. Ed. 2, p. 147.

the light of these considerations it was thought best in the first place to study the applicability of the method of Hart and Andrews in separating and determining inorganic phosphorus from organic phosphorus in water extracts of flesh; and as the objection of Schulze and Castoro to the method of Hart and Andrews is of import, it has been taken into consideration in the following experimental work.

*Experimental Study of the Method of Hart and Andrews.*—A water extract of a sample of raw lean beef round was prepared by the methods described in a former paper[1] from this laboratory. Portions of 250 cc. each of this extract were taken in triplicate and precipitated by the method described by Hart and Andrews. The measured portions of the extract were neutralized to litmus with ammonium hydroxide, 10 grams of crystallized ammonium nitrate were added, and the solutions were placed upon the water-bath. When the temperature of the solutions had reached 65° C., 2 cc. of nitric acid (sp. gr. 1.20) were added, and this addition was followed by 50 cc. of neutral ammonium molybdate solution.

Immediately, a heavy, yellow-green, flocculent precipitate began to separate. After stirring several times, this precipitate settled, leaving a clear filtrate which was of an emerald-green color. The precipitate did not resemble the usual ammonium phosphomolybdate compound, either in color or in form. After standing two hours at room temperature, the precipitate was filtered and washed with a solution of ammonium nitrate. It was then treated with dilute ammonium hydroxide (2.5 per cent.) and hot water. It turned green at once, and was found to be partially insoluble. The resulting solution was dark brown in color and not clear. Upon neutralizing the solution with hydrochloric acid, a grayish flocculent precipitate was produced which was difficultly soluble in strong ammonium hydroxide. Upon adding the magnesia mixture the precipitate formed was flocculent and not of the characteristic nature of the ammonium magnesium phosphate.

Repeated attempts to use the Hart-Andrews method directly upon the water extracts of flesh proved that it could not be so used with accuracy without some modifications. The preliminary experiments indicated that the soluble proteids of

[1] This Journal, 27, 661 (1905).

the extracts were the substances which interfered with the method. This being the case, attempts were made to remove the interfering organic matter by previous precipitation.

In the first place, the precipitant used was neutral ammonium molybdate. To 250 cc. portions of the cold neutral extract, 25 cc. of the neutral molybdate solution were added. A grayish, flocculent precipitate resulted which was removed by filtration after allowing the solution to stand for two hours. The organic matter thus separated was found to contain some phosphorus in every instance. The filtrate from the above, after the addition of 10 grams of ammonium nitrate, was heated to 65° C. Two cc. of nitric acid and 25 cc. of the neutral ammonium molybdate solution were then added. A pale yellow, flocculent precipitate resulted. This ammonium phosphomolybdate precipitate was filtered, washed, and treated as usual for the estimation of phosphorus. The filtrate from this last precipitate remained clear after standing for twenty-four hours. Heating it to 65° C., and then adding 25 cc. of neutral ammonium molybdate did not cause an additional precipitation. However, when 1 cc. of nitric acid was added, a small additional precipitate of ammonium phosphomolybdate was formed. This was removed by filtration and then treated as usual for the determination of phosphorus. The filtrate from this second precipitation gave only a trace of the yellow precipitate upon the addition of another cubic centimeter of nitric acid. It was removed and put with the second precipitate above. The addition of still another cubic centimeter of acid to this last filtrate produced no further separation. The analytical results are given in the table below.

In the second place, an attempt was made to remove the interfering soluble proteid matter by precipitation with ammonium nitrate at a temperature of 65° C. For this purpose 250 cc. portions of the extracts were each treated with 10 grams of ammonium nitrate. The solutions were then heated to 65° C. for fifteen minutes. The resulting gray, flocculent precipitate was separated by filtration after standing for several hours and then washed with ammonium nitrate. This precipitate containing the organic matter, separated by the ammonium nitrate, was treated with ammonium hydroxide and hot water and the amount of phosphorus in the solution was determined as usual. The results proved that there was practically no phosphorus in

combination with the separated organic matter. The filtrate from the above precipitate was heated to 65° C., and 2 cc. of nitric acid and 50 cc. of neutral ammonium molybdate solution were added. The characteristic yellow precipitate began to separate immediately. After allowing the solution to stand three hours, the precipitate was removed by filtration. The resulting filtrate was heated to 65° C., and 25 cc. of neutral ammonium molybdate solution were added. No additional precipitate resulted. The addition of 1 cc. of nitric acid caused the separation of more of the ammonium phosphomolybdate. After the solution had stood for three hours, the precipitate was separated by filtration. The clear filtrate was heated to 65° C., and 1 cc. of nitric acid was again added. A very slight precipitate formed which was removed and the filtrate tested further with another cubic centimeter of acid. The solution now remained perfectly clear. The detailed results of this experiment are given below in Table I.

In the third place, an effort was made to remove the soluble proteid material by coagulation. To do this 500 cc. portions of the cold water extracts of flesh were evaporated upon the water-bath to about 50 cc. The solutions were filtered while hot, and washed thoroughly with hot water. The separated coagula were oxidized in the usual manner and tested for phosphorus. The results indicated clearly that the coagulated proteid matter contained at most only a trace of phosphorus. However, in order to prove conclusively the absence of phosphorus under such circumstances, three different portions of water extracts each from 100 grams of raw flesh were evaporated to about 250 cc., and then filtered. The filtrates were evaporated still further and any coagulable matter which separated was removed and added to the main portion. The coagula were oxidized and the solution tested quantitatively for phosphorus. The results proved that the average amount of phosphorus contained in the coagulated proteid equaled 0.003 per cent., calculated upon the basis of the fresh meat. Since the soluble proteids of flesh coagulable by heat amount to 2.5 per cent. of the fresh meat, the quantity of phosphorus in combination with the coagulated proteid matter equals only 0.12 per cent. of their weight. It is thus evident that the amount of phosphorus held mechanically

or otherwise in the coagula need not be further considered in this connection.

The filtrates from the coagula formed by the evaporation of 500 cc. portions of the original solution were made up to a volume of 200 cc. and neutralized to litmus with ammonium hydroxide. Ten grams of ammonium nitrate were added to the solutions which were then heated to 65° C. Two cc. of nitric acid (sp. gr. 1.20) and 50 cc. of the neutral ammonium molybdate solution were added. The characteristic yellow precipitate was produced, which was removed by filtration. The clear filtrates were heated to 65° C., and upon adding more of the neutral ammonium molybdate solution, they remained perfectly clear. The addition of 1 cc. of nitric acid produced no further precipitate. The addition of another cubic centimeter of acid produced no apparent change.

The following table gives a condensed summary of the results obtained in the preliminary work above described.

TABLE I.—RESULTS OF PRELIMINARY STUDY OF METHODS.

| Laboratory No. | Method. | A, first precipitate. Per cent. | Filtrate from A. B plus 2 cc. $HNO_3$. Per cent. | Filtrate from B. C plus 1 cc. $HNO_3$. Per cent. | Filtrate from C. D plus 1 cc. $HNO_3$. Per cent. | Filtrate from D E plus 1 cc. $HNO_3$. Per cent. | Total inorganic phosphorus (5 cc. $HNO_3$). Per cent. |
|---|---|---|---|---|---|---|---|
| 1811 | Hart-Andrews regular | ..... | 0.044 | 0.062 | none | none | 0.106 |
| 1815 | Hart-Andrews regular | ..... | 0.045 | 0.052 | trace | none | 0.097 |
| 1818 | Hart-Andrews regular | ..... | 0.110 | 0.023 | trace | none | 0.133 |
| | Average (3)..... | ..... | 0.066 | 0.046 | ..... | ..... | 0.112 |
| 1811 | Neutral molybdic solution | 0.015 | 0.134 | 0.024 | trace | none | 0.173 |
| 1815 | Neutral molybdic solution | trace | 0.029 | 0.070 | trace | none | 0.099 |
| 1818 | Neutral molybdic solution | trace | 0.086 | 0.022 | trace | none | 0.108 |
| | Average (3)..... | 0.005 | 0.083 | 0.039 | ..... | ..... | 0.127 |
| 1811 | Ammonium nitrate | none | 0.054 | 0.073 | trace | none | 0.127 |
| 1815 | Ammonium nitrate | none | 0.049 | 0.036 | trace | none | 0.085 |
| 1818 | Ammonium nitrate | trace | 0.089 | 0.036 | trace | none | 0.125 |
| | Average (3)..... | ..... | 0.064 | 0.048 | ..... | ..... | 0.112 |
| 1788 | Evaporation and coagulation | none | 0.125 | none | none | none | 0.125 |
| 1789 | Evaporation and coagulation | none | 0.102 | none | none | none | 0.102 |
| 1811 | Evaporation and coagulation | 0.014 | 0.097 | none | none | none | 0.111 |
| 1815 | Evaporation and coagulation | none | 0.102 | none | none | none | 0.102 |
| 1818 | Evaporation and coagulation | none | 0.111 | none | none | none | 0.111 |
| | Average (last 3) | ..... | 0.103 | ..... | ..... | ..... | 0.108 |

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From a study of data given in this table, it can be seen first, that each of the four methods gives fairly concordant results so far as the amount of total inorganic phosphorus is concerned; second, that the precipitate resulting from the use of the neutral ammonium molybdate solution in the cold and the ammonium nitrate in the hot tends to carry down some phosphorus with it and this necessitates an additional determination; third, that in the method in which the bulk of the organic matter is removed by evaporation, the resulting coagulum contains but a trace of phosphorus; fourth, that the Hart-Andrews method, when applied to the filtrate from the above coagulum, gives the best results, being the only one of the four in which the separation is practically completed by one treatment of nitric acid and ammonium molybdate solution. The filtration of the yellow precipitate, when the latter method is used, is much better and the subsequent washing more rapid and complete than in any of the other methods above mentioned.

In consequence of the results obtained above it was deemed best to use in the future the method last mentioned, which involves the removal of the soluble interfering proteid matter by coagulation. However, a further study of the method was made before finally adopting it. In the first place, it seemed desirable, if possible, to do away with the tedious process of dissolving the pyrophosphate and reprecipitating the phosphorus with the magnesia mixture, which is, of course, necessary when there is any tendency toward reduction by the presence of organic matter. Accordingly, it was thought best to dissolve the yellow ammonium phosphomolybdate in the usual manner with ammonium hydroxide and hot water and then reprecipitate the same from acid solution, as recommended by Woy.[1] The ammoniacal solution of the yellow precipitate was neutralized with nitric acid and diluted to 200 cc. Five grams of ammonium nitrate were added to the solution which was heated to 60° C.; then, while stirring vigorously, 5 cc. of concentrated nitric acid and 20 cc. of acid ammonium molybdate solution were added. The yellow precipitate came down at once without any apparent contamination with organic matter. The filtration was rapid and the filtrate clear.

By this procedure the conditions for the precipitation of the

[1] Chem. Ztg. 21, 442.

phosphorus were brought back to those normally used and in this way no objection could be raised as to the precipitate being contaminated with molybdic acid or ammonium molybdate. Parallel test determinations of this method were made along with that of the official gravimetric method. The following table gives the results.

TABLE II.—RESULTS SHOWING THE INFLUENCE OF THE SOLUTION AND THE REPRECIPITATION OF THE AMMONIUM PHOSPHOMOLYBDATE.

| Laboratory No. | Kind of meat. | Official method. Before dissolving. Per cent. | Official method. After dissolving. Per cent. | Modified method. Per cent. |
|---|---|---|---|---|
| $1837_1$ | Beef rib, roast | 0.095 | 0.087 | 0.089 |
| $1837_2$ | Beef rib, roast | 0.095 | 0.091 | 0.088 |
| $1837_3$ | Beef rib, roast | 0.097 | 0.089 | ..... |
| | Average (3) | 0.096 | 0.089 | 0.089 |
| $1838_1$ | Beef rib, roast | 0.146 | 0.106 | 0.104 |
| $1838_2$ | Beef rib, roast | 0.122 | 0.106 | 0.104 |
| $1838_3$ | Beef rib, roast | 0.118 | 0.102 | ..... |
| | Average (3) | 0.128 | 0.104 | 0.104 |
| | Average, all (6) | 0.112 | 0.097 | 0.097 |

It will be seen by referring to the table, that there is practically no difference in the methods, and inasmuch as the modification makes the work simpler and also considerably shorter, it has been used throughout. Yet, it should be stated that when the ignited pyrophosphate was colored yellow, it was dissolved and reprecipitated.

Again, it was decided to test further the effect of varying amounts of nitric acid to see whether the organic compounds of flesh which contain phosphorus were as stable as the preliminary experiments indicated. For this purpose the following experiment was made upon a water extract of beef flesh. The inorganic phosphorus was precipitated as usual with the neutral ammonium molybdate solution. The filtrates were treated with 10 cc. of concentrated nitric acid, then heated to 60° C. and allowed to stand twenty-four hours. No yellow precipitate was produced. Twenty cc. more of the acid were added and the test repeated. There was no apparent effect produced by this amount of acid, showing that the organic matter was not easily oxidized. It is evident from this experiment that the soluble organic phosphorus compounds of flesh are indeed quite stable even in the presence of considerable excess of nitric acid. Not-

withstanding this fact, it was deemed advisable in the light of the experiment which follows to use the neutral ammonium molybdate solution in the work here reported.

At the same time another portion of the water extract was treated with an acid ammonium molybdate solution, after having removed the coagulum. In this way a direct comparison of the modified Hart-Andrews method was made with the regular official method. In this connection, exactly the same tests were made upon a solution of pure potassium acid phosphate in order to determine if the precipitation by neutral ammonium molybdate in the presence of only 3 cc. of nitric acid (sp. gr. 1.20) was complete.

The following table gives the data obtained in these experiments

TABLE III.—COMPARISON OF THE OFFICIAL METHOD AND THE MODIFIED HART-ANDREWS METHOD.

| | | Official method (acid). | | |
|---|---|---|---|---|
| Laboratory No. | Kind of material. | Before dissolving. Per cent. | After dissolving. Per cent. | Modified method (neutral). Per cent. |
| $1921_1$ | Water extract of beef..... | 0.0125 | ..... | 0.0118 |
| $1921_2$ | Water extract of beef..... | 0.0125 | 0.0120 | 0.0115 |
| $1921_3$ | Water extract of beef..... | 0.0121 | 0.0117 | 0.0116 |
| | Average (3)..... | 0.0124 | 0.0118 | 0.0116 |
| $1922_1$ | Potassium acid phosphate.. | 0.0237 | ..... | 0.0233 |
| $1922_2$ | Potassium acid phosphate.. | 0.0235 | ..... | 0.0233 |
| $1922_3$ | Potassium acid phosphate.. | 0.0230 | ..... | 0.0234 |
| | Average (3)..... | 0.0234 | ..... | 0.0233 |

These results show that the ordinary acid ammonium molybdate solution and the neutral ammonium molybdate solution cause identically the same separation of phosphorus both in cold water extracts of flesh from which the coagulable proteids have been removed and in a solution of potassium dihydrogen phosphate containing no organic matter.

The amount of organic matter present in the above water extracts does not seem to have any more retarding action in the case of the neutral ammonium molybdate where only 3 cc. of nitric acid (sp. gr. 1.20) are present, than it does in the case of the ordinary ammonium molybdate, which is strongly acid. In order to determine still further the influence of the presence of organic matter upon the completeness of the precipitation of the ammonium phosphomolybdate the following test was

made. Two solutions, one of pure potassium acid phosphate and one containing the same amount of potassium acid phosphate mixed with lactic acid, peptone and lactose, were precipitated with neutral ammonium molybdate solution in the presence of only 3 cc. of nitric acid (sp. gr. 1.20). In the first case the average weight of the magnesium pyrophosphate obtained from duplicate determinations amounted to 0.0283 gram and in the latter case, where the precipitation was effected in the presence of organic matter the average weight of the magnesium pyrophosphate equaled 0.0285 gram. These results show that the organic substances above mentioned do not retard the formation of the yellow precipitate. They confirm the results obtained by Hans V. Juptner[1] who maintains that the presence of organic acids does not hinder the precipitation of the ammonium phosphomolybdate.

*Methods Finally Adopted.*—As a result of the above work the following methods were adopted for use in connection with this work. The total phosphorus in the meats and in the water extracts was determined by Neumann's[2] method which has been verified by Sherman.[3] The insoluble phosphorus was ascertained by difference, that is, by subtracting the total soluble phosphorus from the total phosphorus found in the flesh.

Briefly stated, the method used for the determination of the soluble inorganic phosphorus was as follows: 500 cc. portions of the water extract were evaporated upon the water-bath to 50 cc. The coagula were removed by filtration and thoroughly washed with boiling water. The filtrates were treated with 10 grams of ammonium nitrate and warmed upon the water-bath to 60° C. Three cc. of nitric acid (sp. gr. 1.20) and 50 cc. of neutral ammonium molybdate solution were added. During the precipitation the solutions were stirred vigorously. The solutions, after precipitation, were allowed to stand, with frequent stirring, upon the water-bath for fifteen minutes at a temperature of 60° C. They were then removed and allowed to stand in a warm place for two hours. At the end of this period, the precipitates were filtered and washed with a solution of ammonium nitrate as in the determination of the total phosphorus. The yellow precipitates of ammonium phosphomolybdate were dis-

[1] Oesterr. Zeit. Berg. u. Hütten., 1894, p. 471.

[2] Dubois Reymond's Archiv. (Physiol. Abth.), p. 552 (1897).

[3] This Journal, **24**, 1106 (1902).

solved in ammonium hydroxide and hot water. The further details of the method are described above (page 32). The soluble organic phosphorus was obtained by difference, that is, by subtracting the soluble inorganic phosphorus as found immediately above from the total soluble phosphorus of the water extract.

It should be stated here that the volumetric method of Pemberton was tested along with the official gravimetric method, but it was found to be quite unsatisfactory for this work. It was difficult to obtain a definite end reaction with phenolphthalein as the indicator. The results were also found to be lower than those obtained by the use of the gravimetric method.

## PHOSPHORUS CONTENT OF MEATS.

The methods for the determination of the different forms of phosphorus have been used upon samples of flesh, the chemical composition of which has been thoroughly studied in connection with other investigations of this laboratory. As a result, the data regarding the phosphorus content of flesh has been materially reinforced by the analytical results giving the complete composition of the meats. The tables give in detail the results so far obtained in this study.

## DISCUSSION OF RESULTS.

The chemical composition of the meats will be discussed in this connection only so far as the results have to do directly with a consideration of the phosphorus content of flesh, since a paper will soon appear from this laboratory which will include a larger number of analyses of flesh than are presented at this time. Passing therefore directly to the consideration of the phosphorus of flesh it will be seen from the results given in Table VII, that the total phosphorus occurring in the fresh substance of uncooked beef round varies from 0.210 per cent. to 0.345 per cent., the average in the six samples here reported being 0.253 per cent. In these same samples of meat the total phosphorus soluble in cold water ranges from 0.146 to 0.257 per cent., averaging 0.193 per cent. The phosphorus in the form of compounds insoluble in cold water, in the fresh substance of uncooked beef round varies from 0.035 to 0.088 per cent., the average being 0.060 per cent. The soluble phosphorus in the form of inorganic substances, chiefly phosphates of potassium, ranges from 0.090 to 0.153 per cent. of the fresh substance of the beef round. The

average per cent. of phosphorus in this form equals 0.120. The phosphorus in the form of soluble organic matter varies from 0.043 to 0.104 per cent., the average being 0.073 per cent.

By referring to the same table, it will be seen that in nine different cuts of veal taken from the same animal, the total phosphorus varies from 0.168 to 0.269 per cent.; the total soluble phosphorus ranges from 0.112 to 0.157 per cent.; the insoluble phosphorus varies from 0.053 to 0.136 per cent.; the soluble inorganic phosphorus ranges from 0.075 to 0.118 per cent. while the soluble organic phosphorus varies from 0.018 to 0.041 per cent. The average results for the fresh substance of the nine samples of veal are as follows: Total phosphorus 0.202, total soluble phosphorus 0.128, insoluble phosphorus 0.074, soluble inorganic phosphorus 0.095, and soluble organic phosphorus 0.032 per cent.

From the average results given above for the beef and for the veal, it is evident that the phosphorus content of the samples of beef is greater than it is in those of the veal. This difference between the two kinds of meat is most marked in the case of the soluble organic phosphorus, which is 2.3 times greater in the beef than in the veal. All the other forms of phosphorus are greater in beef flesh than in veal flesh with one exception; namely, the insoluble phosphorus, which is somewhat greater in the veal than it is in the beef. These variations in the phosphorus content of the two kinds of flesh are not due to the difference in the quantities of water and fat which they contain. That this is true, may be readily observed by referring to Tables VIII and IX in which the results are calculated to the water-free basis and to the water-free and fat-free substance. In the former case, the average soluble organic phosphorus in the beef equals 0.285 per cent. while in the veal it amounts to only 0.110 per cent. That is to say, this form of phosphorus existing in the samples of beef is 2.6 times greater than that occurring in the samples of veal. Expressed upon the basis of the water-free and fat-free substance the total soluble phosphorus in the beef flesh is equal to 0.835 per cent. while it forms only 0.607 per cent. of the water-free substance of the veal.

At first sight, it would appear, perhaps, that this difference in the quantities of phosphorus in the two kinds of meat was due to the difference in the amount of fat which they contain; since

TABLE IV.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO FRESH SUBSTANCE.

| Laboratory No. | Kind of meat. | Water. Per cent. | Dry substance (direct.) Per cent. | Fat. Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Nitrogen. Soluble. Per cent. | Nitrogen. Insoluble. Per cent. | Nitrogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 73.42 | 27.40 | 3.15 | 2.42 | 17.96 | 20.38 | 2.78 | 0.87 | 0.22 | 1.09 | 0.7798 | 2.8732 | 3.6530 |
| 1789 | Beef round, raw | 74.53 | 26.10 | 3.59 | 2.42 | 16.35 | 18.77 | 2.68 | 0.95 | 0.11 | 1.06 | 0.7480 | 2.6170 | 3.3650 |
| 1823 | Beef round, raw | 75.61 | 24.41 | 2.14 | 2.42 | 15.97 | 18.39 | 2.80 | 1.00 | 0.08 | 1.08 | 0.7885 | 2.5555 | 3.3440 |
| 1828 | Beef round, raw | 75.69 | 24.95 | 2.52 | 2.21 | 16.40 | 18.61 | 2.76 | 0.94 | 0.12 | 1.06 | 0.7377 | 2.6243 | 3.3620 |
| 1849 | Beef round, raw | 74.22 | 26.29 | 2.46 | 2.97 | 16.61 | 19.58 | 3.15 | 0.99 | 0.11 | 1.10 | 0.8884 | 2.6566 | 3.5450 |
| 1850 | Beef round, raw | 74.89 | 25.26 | 2.24 | 2.93 | 15.67 | 18.60 | 3.34 | 0.99 | 0.09 | 1.08 | 0.8998 | 2.5062 | 3.4060 |
| | Average (6) | 74.73 | 25.74 | 2.68 | 2.57 | 16.49 | 19.06 | 2.92 | 0.96 | 0.12 | 1.08 | 0.8070 | 2.6388 | 3.4458 |
| 1853 | Veal shank, raw | 75.08 | 25.44 | 3.03 | 2.07 | 17.39 | 19.46 | 1.93 | 0.66 | 0.36 | 1.02 | 0.5687 | 2.7823 | 3.3510 |
| 1854 | Veal chuck, raw | 72.93 | 27.98 | 6.33 | 1.81 | 16.71 | 18.52 | 2.13 | 0.67 | 0.33 | 1.00 | 0.5536 | 2.6734 | 3.2270 |
| 1855 | Veal ribs, raw | 68.38 | 31.91 | 12.09 | 1.74 | 14.64 | 16.38 | 2.47 | 0.67 | 0.30 | 0.97 | 0.5904 | 2.3436 | 2.9340 |
| 1856 | Veal shoulder, raw | 71.00 | 29.29 | 8.57 | 1.88 | 15.43 | 17.31 | 2.37 | 0.74 | 0.30 | 1.04 | 0.5988 | 2.4682 | 3.0670 |
| 1857 | Veal breast, raw | 63.34 | 36.65 | 16.66 | 1.79 | 15.10 | 16.89 | 2.20 | 0.66 | 0.24 | 0.90 | 0.5367 | 2.4163 | 2.9530 |
| 1858 | Veal loin, raw | 68.08 | 31.40 | 10.95 | 1.79 | 15.24 | 17.03 | 2.44 | 0.74 | 0.24 | 0.98 | 0.6001 | 2.4389 | 3.0390 |
| 1859 | Veal flank, raw | 64.18 | 36.38 | 16.13 | 1.84 | 15.38 | 17.22 | 2.08 | 0.78 | 0.17 | 0.95 | 0.5889 | 2.4611 | 3.0500 |
| 1860 | Veal leg, raw | 73.40 | 26.04 | 3.76 | 1.83 | 16.28 | 18.11 | 3.08 | 0.89 | 0.20 | 1.09 | 0.6790 | 2.6050 | 3.2840 |
| 1861 | Veal hind shank, raw | 73.36 | 27.24 | 5.03 | 1.94 | 16.84 | 18.78 | 2.40 | 0.76 | 0.27 | 1.03 | 0.6257 | 2.6943 | 3.3200 |
| | Average (9) | 69.97 | 30.26 | 9.17 | 1.85 | 15.89 | 17.74 | 2.35 | 0.73 | 0.27 | 1.00 | 0.5935 | 2.5426 | 3.1361 |
| 1801 | Beef round, boiled | 61.26 | 39.69 | 3.54 | 0.14 | 34.43 | 34.57 | 1.00 | 0.34 | 0.24 | 0.58 | 0.1769 | 5.5091 | 5.6860 |
| 1807 | Beef round, boiled | 64.44 | 36.35 | 2.97 | 0.25 | 31.67 | 31.92 | 0.97 | 0.31 | 0.18 | 0.49 | 0.1816 | 5.0674 | 5.2490 |
| 1808 | Beef round, boiled | 61.70 | 39.00 | 3.65 | 0.33 | 33.45 | 33.78 | 1.01 | 0.42 | 0.14 | 0.56 | 0.2038 | 5.3512 | 5.5550 |

TABLE IV.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO FRESH SUBSTANCE—*Continued.*

| Laboratory No. | Kind of meat. | Water. Per cent. | Dry substance (direct). Per cent. | Fat. Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Ntirogen. Soluble. Per cent. | Ntirogen. Insoluble. Per cent. | Ntirogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1802 | Beef round, boiled | 59.54 | 41.44 | 3.92 | 0.18 | 35.65 | 35.83 | 1.12 | 0.31 | 0.26 | 0.57 | 0.1823 | 5.7037 | 5.8860 |
| 1824 | Beef round, boiled | 55.96 | 44.60 | 8.47 | 0.40 | 33.01 | 33.41 | 1.89 | 0.62 | 0.21 | 0.83 | 0.3046 | 5.3064 | 5.6110 |
| 1809 | Beef round, boiled | 60.61 | 40.12 | 3.53 | 1.04 | 33.72 | 34.76 | 1.21 | 0.44 | 0.18 | 0.62 | 0.3472 | 5.3948 | 5.7420 |
| 1803 | Beef round, boiled | 58.94 | 41.62 | 3.60 | 0.52 | 35.68 | 36.20 | 1.22 | 0.42 | 0.18 | 0.60 | 0.2534 | 5.7096 | 5.9630 |
| | Average (7) | 60.35 | 40.40 | 4.24 | 0.41 | 33.94 | 34.35 | 1.20 | 0.41 | 0.20 | 0.61 | 0.2357 | 5.4346 | 5.6703 |
| 1825 | Beef round, pot roast | 56.92 | 44.35 | 5.58 | 0.37 | 34.32 | 34.69 | 2.84 | 1.03 | 0.21 | 1.24 | 0.4783 | 5.4907 | 5.9690 |
| 1829 | Beef round, pot roast | 57.57 | 42.85 | 4.20 | 0.46 | 35.14 | 35.60 | 2.10 | 0.68 | 0.27 | 0.95 | 0.3953 | 5.6227 | 6.0180 |
| 1830 | Beef round, pot roast | 61.65 | 38 80 | 4.79 | 0.41 | 31.06 | 31.47 | 1.80 | 0.54 | 0.20 | 0.74 | 0.3365 | 4.9695 | 5.3060 |
| | Average (3) | 58.71 | 42.00 | 4.86 | 0.41 | 33.51 | 33.92 | 2.25 | 0.75 | 0.23 | 0.98 | 0.4034 | 5.3609 | 5.7643 |
| 1831 | Beef rib, roast | 44.78 | 55.08 | 36.84 | 0.52 | 15.30 | 15.82 | 1.59 | 0.65 | 0.18 | 0.83 | 0.3300 | 2.4490 | 2.7790 |
| 1833 | Beef rib, roast | 47.33 | 52.33 | 32.11 | 0.57 | 16.84 | 17.41 | 2.01 | 0.65 | 0.15 | 0.80 | 0.3678 | 2.6922 | 3.0600 |
| 1837 | Beef rib, roast | 53.33 | 47.07 | 25.21 | 0.48 | 18.56 | 19.04 | 1.93 | 0.77 | 0.12 | 0.89 | 0.3671 | 2.9709 | 3.3380 |
| 1838 | Beef rib, roast | 49.73 | 50.67 | 27.79 | 0.38 | 19.65 | 20.03 | 1.95 | 0.71 | 0.19 | 0.90 | 0.3520 | 3.1440 | 3.4960 |
| 1840 | Beef rib, roast | 42.35 | 58.07 | 37.16 | 0.33 | 18.04 | 18.37 | 1.77 | 0.66 | 0.11 | 0.77 | 0.3086 | 2.8874 | 3.1960 |
| 1848 | Beef rib, roast | lost | .... | lost | 0.36 | 21.47 | 21.83 | 2.25 | 0.83 | 0.20 | 1.03 | 0.3981 | 3.4339 | 3.8320 |
| 1842 | Beef rib, roast | 45.73 | 54.64 | 35.19 | 0.31 | 16.44 | 16.75 | 1.82 | 0.67 | 0.21 | 0.88 | 0.3207 | 2.6303 | 2.9510 |
| 1844 | Beef rib, roast | 42.15 | 58.25 | 34.42 | 0.27 | 20.65 | 20.92 | 1.90 | 0.70 | 0.31 | 1.01 | 0.3271 | 3.3039 | 3.6310 |
| 1846 | Beef rib, roast | 45.63 | 55.10 | 27.60 | 0.25 | 23.59 | 23.84 | 2.60 | 0.44 | 0.62 | 1.06 | 0.3902 | 3.7748 | 4.1650 |
| | Average (9) | 46.38 | 53.90 | 32.04 | 0.39 | 18.94 | 19.33 | 1.98 | 0.68 | 0.23 | 0.91 | 0.3513 | 3.0318 | 3.3831 |

TABLE V.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO WATER-FREE SUBSTANCE.

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Fat. Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Nitrogen. Soluble. Per cent. | Nitrogen. Insoluble. Per cent. | Nitrogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 100.00 | 11.50 | 8.83 | 65.55 | 74.38 | 10.15 | 3.18 | 0.80 | 3.98 | 2.846 | 10.486 | 13.332 |
| 1789 | Beef round, raw | 100.00 | 13.75 | 9.27 | 62.65 | 71.92 | 10.27 | 3.64 | 0.42 | 4.06 | 2.866 | 10.027 | 12.893 |
| 1823 | Beef round, raw | 100.00 | 8.77 | 9.91 | 65.42 | 75.33 | 11.47 | 4.10 | 0.33 | 4.42 | 3.230 | 10.467 | 13.699 |
| 1828 | Beef round, raw | 100.00 | 10.10 | 8.86 | 65.73 | 74.59 | 11.06 | 3.77 | 0.48 | 4.25 | 2.957 | 10.518 | 13.475 |
| 1849 | Beef round, raw | 100.00 | 9.36 | 11.30 | 63.18 | 74.48 | 11.98 | 3.76 | 0.42 | 4.18 | 3.379 | 10.105 | 13.484 |
| 1850 | Beef round, raw | 100.00 | 8.87 | 11.60 | 62.03 | 73.63 | 13.22 | 3.92 | 0.36 | 4.28 | 3.562 | 9.922 | 13.484 |
| | Average (6) | 100.00 | 10.39 | 9.96 | 64.10 | 74.06 | 11.36 | 3.73 | 0.47 | 4.20 | 3.140 | 10.255 | 13.395 |
| 1853 | Veal shank, raw | 100.00 | 11.91 | 8.14 | 68.36 | 76.49 | 7.59 | 2.59 | 1.42 | 4.01 | 2.235 | 10.937 | 13.172 |
| 1854 | Veal chuck, raw | 100.00 | 22.62 | 6.47 | 59.72 | 66.19 | 7.61 | 2.39 | 1.18 | 3.57 | 1.979 | 9.554 | 11.533 |
| 1855 | Veal ribs, raw | 100.00 | 37.89 | 5.45 | 45.88 | 51.33 | 7.74 | 2.10 | 0.94 | 3.04 | 1.850 | 7.344 | 9.194 |
| 1856 | Veal shoulder, raw | 100.00 | 29.26 | 6.42 | 52.68 | 69.10 | 8.10 | 2.53 | 1.02 | 3.55 | 2.044 | 8.427 | 10.471 |
| 1857 | Veal breast, raw | 100.00 | 45.45 | 4.88 | 41.20 | 46.08 | 6.00 | 1.81 | 0.65 | 2.46 | 1.464 | 6.593 | 8.057 |
| 1858 | Veal loin, raw | 100.00 | 34.87 | 5.70 | 48.54 | 54.24 | 7.77 | 2.36 | 0.76 | 3.12 | 1.911 | 7.767 | 9.678 |
| 1859 | Veal flank, raw | 100.00 | 44.34 | 5.06 | 42.28 | 47.34 | 5.72 | 2.14 | 0.47 | 2 61 | 1.619 | 6.765 | 8.384 |
| 1860 | Veal leg, raw | 100.00 | 14.44 | 7.03 | 62.52 | 69.55 | 11.83 | 3.42 | 0.77 | 4.19 | 2.608 | 10.003 | 12.611 |
| 1861 | Veal hind shank, raw | 100.00 | 18.47 | 7.12 | 61.82 | 68.94 | 8.81 | 2.79 | 0.99 | 3.78 | 2.297 | 9.891 | 12.188 |
| | Average (9) | 100.00 | 28.81 | 6.25 | 53.67 | 59.92 | 7.91 | 2.46 | 0.91 | 3.37 | 2.001 | 8.586 | 10.587 |
| 1801 | Beef round, boiled | 100.00 | 8.92 | 0.35 | 86.75 | 87.10 | 2.52 | 0.86 | 0.60 | 1.46 | 0.446 | 13.880 | 14.326 |
| 1807 | Beef round, boiled | 100.00 | 8.17 | 0.69 | 87.13 | 87.81 | 2.67 | 0.85 | 0.50 | 1.35 | 0.500 | 13.940 | 14.440 |
| 1808 | Beef round, boiled | 100.00 | 9.36 | 0.85 | 85.77 | 86.62 | 2.59 | 1.08 | 0.36 | 1.44 | 0.522 | 13.721 | 14.243 |

TABLE V.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO WATER-FREE SUBSTANCE—*Continued.*

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Fat. Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Nitrogen. Soluble. Per cent. | Nitrogen. Insoluble. Per cent. | Nitrogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1802 | Beef round, boiled | 100.00 | 9.46 | 0.44 | 86.03 | 86.46 | 2.70 | 0.75 | 0.63 | 1.38 | 0.440 | 13.764 | 14.204 |
| 1824 | Beef round, boiled | 100.00 | 18.99 | 0.90 | 74.01 | 74.91 | 4.24 | 1.39 | 0.47 | 1.86 | 0.683 | 11.898 | 12.581 |
| 1809 | Beef round, boiled | 100.00 | 8.80 | 2.59 | 84.05 | 86.64 | 3.02 | 1.10 | 0.45 | 1.55 | 0.865 | 13.447 | 14.312 |
| 1803 | Beef round, boiled | 100.00 | 8.65 | 1.25 | 85.73 | 86.98 | 2.93 | 1.01 | 0.43 | 1.44 | 0.609 | 13.718 | 14.327 |
| | Average (7) | 100.00 | 10.34 | 1.01 | 84.21 | 85.22 | 2.95 | 1.01 | 0.49 | 1.50 | 0.581 | 13.481 | 14.062 |
| 1825 | Beef round, pot roast | 100.00 | 12.58 | 0.83 | 77.39 | 78.22 | 6.40 | 2.32 | 0.48 | 2.80 | 1.079 | 12 380 | 13.459 |
| 1829 | Beef round, pot roast | 100.00 | 9.80 | 1.07 | 82.01 | 83.08 | 4.90 | 1.59 | 0.63 | 2.22 | 0.922 | 13.122 | 14.044 |
| 1830 | Beef round, pot roast | 100.00 | 12.35 | 1.06 | 80.05 | 81.11 | 4.64 | 1.40 | 0.51 | 1.91 | 0.867 | 12.808 | 13.675 |
| | Average (3) | 100.00 | 11.58 | 0.99 | 79.81 | 80.80 | 5.31 | 1.77 | 0.54 | 2.31 | 0.956 | 12.770 | 13.726 |
| 1831 | Beef rib, roast | 100.00 | 66.88 | 0.94 | 27.78 | 28.72 | 2.89 | 1.18 | 0.33 | 1.51 | 0.600 | 4.445 | 5.045 |
| 1833 | Beef rib, roast | 100.00 | 61.36 | 1.09 | 32.18 | 32.27 | 3.83 | 1.24 | 0.29 | 1.53 | 0.703 | 5.145 | 5.848 |
| 1837 | Beef rib, roast | 100.00 | 53.54 | 1.02 | 39.43 | 40.45 | 4.10 | 1.64 | 0.25 | 1.89 | 0.780 | 6.312 | 7.092 |
| 1838 | Beef rib, roast | 100.00 | 54.85 | 0.75 | 38.78 | 39.53 | 3.85 | 1.40 | 0.38 | 1.78 | 0.694 | 6.205 | 6.899 |
| 1840 | Beef rib, roast | 100.00 | 63.99 | 0.57 | 31.07 | 31.64 | 3.05 | 1.14 | 0.19 | 1.33 | 0.531 | 4.973 | 5.504 |
| 1842 | Beef rib, roast | 100.00 | 64.43 | 0.57 | 30.09 | 30.66 | 3.33 | 1.23 | 0.38 | 1.61 | 0.587 | 4.814 | 5.401 |
| 1844 | Beef rib, roast | 100.00 | 59.09 | 0.46 | 35.45 | 35.91 | 3.27 | 1.20 | 0.53 | 1.73 | 0.562 | 5.672 | 6.234 |
| 1846 | Beef rib, roast | 100.00 | 50.09 | 0.45 | 42.81 | 43.27 | 4.72 | 0.80 | 1.13 | 1.93 | 0.708 | 6.851 | 7.559 |
| | Average (8) | 100.00 | 59.28 | 0.73 | 34.70 | 35.43 | 3.63 | 1.23 | 0.43 | 1.66 | 0.646 | 5.552 | 6.198 |

TABLE VI.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO WATER- AND FAT-FREE SUBSTANCE.

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Nitrogen. Soluble. Per cent. | Nitrogen. Insoluble. Per cent. | Nitrogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 100.00 | 9.98 | 74.06 | 84.04 | 11.46 | 3.59 | 0.90 | 4.49 | 3.216 | 11.848 | 15.064 |
| 1789 | Beef round, raw | 100.00 | 10.75 | 72.63 | 83.38 | 11.91 | 4.22 | 0.49 | 4.71 | 3.323 | 11.626 | 14.949 |
| 1823 | Beef round, raw | 100.00 | 10.87 | 71.71 | 82.58 | 12.58 | 4.49 | 0.36 | 4.85 | 3.541 | 11.475 | 15.016 |
| 1828 | Beef round, raw | 100.00 | 9.85 | 73.12 | 82.97 | 12.30 | 4.19 | 0.54 | 4.73 | 3.289 | 11.700 | 14.989 |
| 1849 | Beef round, raw | 100.00 | 12.46 | 69.70 | 82.16 | 13.22 | 4.15 | 0.46 | 4.62 | 3.728 | 11.148 | 14.876 |
| 1850 | Beef round, raw | 100.00 | 12.73 | 68.07 | 80.80 | 14.51 | 4.30 | 0.39 | 4.69 | 3.909 | 10.887 | 14.796 |
| | Average (6) | 100.00 | 11.11 | 71.55 | 82.66 | 12.66 | 4.16 | 0.52 | 4.68 | 3.501 | 11.447 | 14.948 |
| 1853 | Veal shank, raw | 100.00 | 9.24 | 77.60 | 86.84 | 8.61 | 2.94 | 1.61 | 4.55 | 2.538 | 12.415 | 14.953 |
| 1854 | Veal chuck, raw | 100.00 | 8.36 | 77.18 | 85.54 | 9.84 | 3.09 | 1.52 | 4.62 | 2.557 | 12.348 | 14.905 |
| 1855 | Veal ribs, raw | 100.00 | 8.78 | 73.86 | 82.64 | 12.46 | 3.38 | 1.51 | 4.89 | 2.979 | 11.824 | 14.803 |
| 1856 | Veal shoulder, raw | 100.00 | 9.07 | 74.47 | 83.54 | 11.44 | 3.57 | 1.45 | 5.03 | 2.890 | 11.912 | 14.802 |
| 1857 | Veal breast, raw | 100.00 | 8.95 | 75.54 | 84.49 | 11.01 | 3.30 | 1.20 | 4.50 | 2.685 | 12.088 | 14.773 |
| 1858 | Veal loin raw | 100.00 | 8.75 | 74.52 | 83.27 | 11.93 | 3.62 | 1.17 | 4.79 | 2.935 | 11.926 | 14.861 |
| 1859 | Veal flank, raw | 100.00 | 9.09 | 75.95 | 85.04 | 10.27 | 3.85 | 0.84 | 4.69 | 2.908 | 12.154 | 15.062 |
| 1860 | Veal leg, raw | 100.00 | 8.21 | 73.07 | 81.28 | 13.82 | 3.99 | 0.90 | 4.89 | 3.048 | 11.692 | 14.740 |
| 1861 | Veal hind shank, raw | 100.00 | 8.74 | 75.82 | 84.56 | 10.81 | 3.42 | 1.22 | 4.64 | 2.817 | 12.131 | 14.948 |
| | Average (9) | 100.00 | 8.80 | 75.33 | 84.13 | 11.13 | 3.46 | 1.27 | 4.73 | 2.817 | 12.055 | 14.872 |
| 1801 | Beef round, boiled | 100.00 | 0.39 | 95.24 | 95.63 | 2.77 | 0.94 | 0.66 | 1.60 | 0.489 | 15.240 | 15.729 |
| 1807 | Beef round, boiled | 100.00 | 0.75 | 94.88 | 95.63 | 2.91 | 0.93 | 0.54 | 1.47 | 0.544 | 15.181 | 15.725 |
| 1808 | Beef round, boiled | 100.00 | 0.93 | 94.63 | 95.56 | 2.86 | 1.19 | 0.40 | 1.58 | 0.576 | 15.138 | 15.714 |

TABLE VI.—CHEMICAL COMPOSITION OF MEATS CALCULATED TO WATER- AND FAT-FREE SUBSTANCE—*Continued.*

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Proteid. Soluble. Per cent. | Proteid. Insoluble. Per cent. | Proteid. Total. Per cent. | Organic extractives. Per cent. | Ash. Soluble. Per cent. | Ash. Insoluble. Per cent. | Ash. Total. Per cent. | Nitrogen. Soluble. Per cent. | Nitrogen. Insoluble. Per cent. | Nitrogen. Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1802 | Beef round, boiled | 100.00 | 0.48 | 95.02 | 95.50 | 2.99 | 0.83 | 0.69 | 1 52 | 0.486 | 15.202 | 15.688 |
| 1824 | Beef round, boiled | 100.00 | 1.11 | 91.36 | 92.47 | 5.23 | 1.72 | 0.58 | 2.30 | 0.843 | 14.687 | 15.530 |
| 1809 | Beef round, boiled | 100.00 | 2.84 | 92.16 | 95.00 | 3.31 | 1.20 | 0.49 | 1.69 | 0.949 | 14.744 | 15.693 |
| 1803 | Beef round, boiled | 100.00 | 1.37 | 93.84 | 95.21 | 3.21 | 1.10 | 0.48 | 1.58 | 0.667 | 15.017 | 15.684 |
| | Average (7) | 100.00 | 1.12 | 93.88 | 95.00 | 3.32 | 1.13 | 0.55 | 1.68 | 0.650 | 15.030 | 15.680 |
| 1825 | Beef round, pot roast | 100.00 | 0.96 | 88.52 | 89.48 | 7.33 | 2.66 | 0.54 | 3.20 | 1.234 | 14.162 | 15.396 |
| 1829 | Beef round, pot roast | 100.00 | 1.19 | 90.92 | 92.11 | 5.43 | 1.76 | 0.70 | 2.46 | 1.023 | 14.548 | 15.571 |
| 1830 | Beef round, pot roast | 100.00 | 1.21 | 91.33 | 92.54 | 5.29 | 1.59 | 0.59 | 2.18 | 0.989 | 14.612 | 15.601 |
| | Average (3) | 100.00 | 1.12 | 90.26 | 91.38 | 6.02 | 2.00 | 0.61 | 2.61 | 1.082 | 14.441 | 15.523 |
| 1831 | Beef rib, roast | 100.00 | 2.85 | 83.88 | 86.73 | 8.72 | 3.56 | 0.99 | 4.55 | 1.809 | 13.427 | 15.286 |
| 1833 | Beef rib, roast | 100.00 | 2.82 | 83.28 | 86.10 | 9.94 | 3.21 | 0.75 | 3.96 | 1.819 | 13.315 | 15.134 |
| 1837 | Beef rib, roast | 100.00 | 2.20 | 84.90 | 87.10 | 8.83 | 3.52 | 0.55 | 4.07 | 1.679 | 13.591 | 15.270 |
| 1838 | Beef rib, roast | 100.00 | 1.66 | 89.88 | 91.54 | 8.52 | 3.10 | 0.83 | 3.93 | 1.538 | 13.741 | 15.279 |
| 1840 | Beef rib, roast | 100.00 | 1.58 | 86.28 | 87.86 | 8.46 | 3.15 | 0.53 | 3.68 | 1.476 | 13.809 | 15.285 |
| 1842 | Beef rib, roast | 100.00 | 1.59 | 84.52 | 86.12 | 9.36 | 3.44 | 1.08 | 4.52 | 1.649 | 13.523 | 15.172 |
| 1844 | Beef rib, roast | 100.00 | 1.13 | 86.66 | 87.79 | 7.97 | 2.94 | 1.30 | 4.24 | 1.372 | 13.865 | 15.237 |
| 1846 | Beef rib, roast | 100.00 | 0.91 | 85.78 | 86.69 | 9.45 | 1.60 | 2.25 | 3.85 | 1.419 | 13.726 | 15.145 |
| | Average (8) | 100.00 | 1.84 | 85.65 | 87.49 | 8.91 | 3.07 | 1.03 | 4.10 | 1.595 | 13.624 | 15.219 |

TABLE VII.—FORMS OF PHOSPHORUS IN MEATS CALCULATED TO FRESH SUBSTANCE.

| Laboratory No. | Kind of meat. | Water. Per cent. | Dry substance (direct). Per cent. | Fat. Per cent. | Phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 73.42 | 27.40 | 3.15 | 0.125 | 0.043 | 0.168 | 0.052 | 0.220 |
| 1789 | Beef round, raw | 74.53 | 26.10 | 3.59 | 0.102 | 0.044 | 0.146 | 0.064 | 0.210 |
| 1823 | Beef round, raw | 75.61 | 24.41 | 2.14 | 0.090 | 0.097 | 0.187 | 0.035 | 0.222 |
| 1828 | Beef round, raw | 75.69 | 24.95 | 2.52 | 0.102 | 0.048 | 0 150 | 0.060 | 0.310 |
| 1849 | Beef round, raw | 74.22 | 26.29 | 2.46 | 0.148 | 0.101 | 0.249 | 0.062 | 0.311 |
| 1850 | Beef round, raw | 74.89 | 25.26 | 2.24 | 0.153 | 0.104 | 0.257 | 0.088 | 0.345 |
| | Average (6) | 74.73 | 25.74 | 2.68 | 0.120 | 0.073 | 0.193 | 0.060 | 0.253 |
| 1853 | Veal shank, raw | 75.08 | 25.44 | 3.03 | 0.088 | 0.035 | 0.123 | 0.054 | 0.177 |
| 1854 | Veal chuck, raw | 72.93 | 27.98 | 6.33 | 0.087 | 0.036 | 0.123 | 0.070 | 0.193 |
| 1855 | Veal ribs, raw | 68.38 | 31.91 | 12.09 | 0.094 | 0.033 | 0.127 | 0.109 | 0.236 |
| 1856 | Veal shoulder, raw | 71.50 | 29.29 | 8.57 | 0.102 | 0.031 | 0.133 | 0.136 | 0.269 |
| 1857 | Veal breast, raw | 63.34 | 36.65 | 16.66 | 0.075 | 0.037 | 0.112 | 0.056 | 0.168 |
| 1858 | Veal loin, raw | 68.08 | 31.40 | 10.95 | 0.092 | 0.041 | 0.133 | 0.053 | 0.186 |
| 1859 | Veal flank, raw | 64.18 | 36.38 | 16.13 | 0.094 | 0.018 | 0.112 | 0.053 | 0.175 |
| 1860 | Veal leg, raw | 73.40 | 26.04 | 3.76 | 0.118 | 0.039 | 0.157 | 0.064 | 0.221 |
| 1861 | Veal hind shank, raw | 73.36 | 27.24 | 5.03 | 0.109 | 0.023 | 0.132 | 0.059 | 0.191 |
| | Average (9) | 69.97 | 30.26 | 9.17 | 0.095 | 0.032 | 0.128 | 0.074 | 0.202 |
| 1801 | Beef round, boiled | 61.26 | 39.69 | 3.54 | .... | .... | 0.075 | 0.087 | 0.162 |
| 1807 | Beef round, boiled | 64.44 | 36.35 | 2.97 | .... | .... | 0.067 | 0.076 | 0.143 |
| 1808 | Beef round, boiled | 61.70 | 39.00 | 3.65 | .... | .... | 0.068 | 0.094 | 0.162 |

TABLE VII.—FORMS OF PHOSPHORUS IN MEATS CALCULATED TO FRESH SUBSTANCE—*Continued.*

| Laboratory No. | Kind of meat. | Water. Per cent. | Dry substance (direct.). Per cent. | Fat. Per cent. | Phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|
| 1802 | Beef round, boiled | 59.54 | 41.44 | 3.92 | .... | .... | 0.073 | 0.094 | 0.167 |
| 1824 | Beef round, boiled | 55.96 | 44.60 | 8.47 | 0.085 | 0.041 | 0.126 | 0.087 | 0.213 |
| 1809 | Beef round, boiled | 60.61 | 40.12 | 3.53 | .... | .... | 0.081 | 0.080 | 0.161 |
| 1803 | Beef round, boiled | 58.94 | 41.62 | 3.60 | .... | .... | 0.081 | 0.086 | 0.167 |
| | Average (7) | 60.35 | 40.40 | 4.24 | .... | .... | 0.082 | 0.086 | 0.168 |
| 1825 | Beef round, pot roast | 56.92 | 44.35 | 5.58 | 0.122 | 0.059 | 0.181 | 0.083 | 0.264 |
| 1829 | Beef round, pot roast | 57.57 | 42.85 | 4.20 | 0.112 | 0.049 | 0.161 | 0.066 | 0.227 |
| 1830 | Beef round, pot roast | 61.65 | 38.80 | 4.79 | 0.104 | 0.018 | 0.122 | 0.103 | 0.225 |
| | Average (3) | 58.71 | 42.00 | 4.86 | 0.113 | 0.042 | 0.155 | 0.084 | 0.239 |
| 1831 | Beef rib, roast | 44.78 | 55.08 | 36.84 | 0.095 | 0.023 | 0.118 | 0.030 | 0.148 |
| 1833 | Beef rib, roast | 47.33 | 52.33 | 32.11 | 0.089 | 0.035 | 0.124 | 0.034 | 0.158 |
| 1837 | Beef rib, roast | 53.33 | 47.07 | 25.21 | 0.089 | 0.039 | 0.128 | 0.059 | 0.187 |
| 1838 | Beef rib, roast | 49.73 | 50.67 | 27.79 | 0.104 | 0.044 | 0.148 | 0.042 | 0.190 |
| 1840 | Beef rib, roast | 42.35 | 58.07 | 37.16 | 0.081 | 0.038 | 0.119 | 0.048 | 0.167 |
| 1848 | Beef rib, roast | lost | .... | lost | 0.102 | 0.047 | 0.149 | 0.049 | 0.198 |
| 1842 | Beef rib, roast | 45.73 | 54.64 | 35.19 | 0.090 | 0.032 | 0.122 | 0.037 | 0.159 |
| 1844 | Beef rib, roast | 42.15 | 58.25 | 34.42 | 0.097 | 0.042 | 0.139 | 0.054 | 0.193 |
| 1846 | Beef rib, roast | 45.63 | 55.10 | 27.60 | 0.120 | 0.038 | 0.158 | 0.056 | 0.214 |
| | Average (9) | 46.38 | 53.90 | 32.04 | 0.096 | 0.038 | 0.134 | 0.045 | 0.179 |

TABLE VIII.—FORMS OF PHOSPHORUS IN MEATS CALCULATED TO WATER-FREE SUBSTANCE.

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Fat. Per cent. | Phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw..... | 100.00 | 11.50 | 0.456 | 0.157 | 0.613 | 0.190 | 0.803 |
| 1789 | Beef round, raw..... | 100.00 | 13.75 | 0.391 | 0.169 | 0.560 | 0.245 | 0.805 |
| 1823 | Beef round, raw..... | 100.00 | 8.77 | 0.369 | 0.397 | 0.766 | 0.143 | 0.909 |
| 1828 | Beef round, raw..... | 100.00 | 10.10 | 0.409 | 0.192 | 0.601 | 0.240 | 0.841 |
| 1849 | Beef round, raw..... | 100.00 | 9.36 | 0.563 | 0.384 | 0.947 | 0.236 | 1.183 |
| 1150 | Beef round, raw..... | 100.00 | 8.87 | 0.606 | 0.411 | 1.017 | 0.348 | 1.366 |
| | Average (6)..... | 100.00 | 10.39 | 0.466 | 0.285 | 0.751 | 0.234 | 0.985 |
| 1853 | Veal shank, raw..... | 100.00 | 11.91 | 0.346 | 0.138 | 0.484 | 0.212 | 0.696 |
| 1854 | Veal chuck, raw..... | 100.00 | 22.62 | 0.311 | 0.129 | 0.440 | 0.250 | 0.690 |
| 1855 | Veal ribs, raw..... | 100.00 | 37.89 | 0.295 | 0.103 | 0.398 | 0.341 | 0.740 |
| 1856 | Veal shoulder, raw..... | 100.00 | 29.26 | 0.349 | 0.106 | 0.455 | 0.465 | 0.920 |
| 1857 | Veal breast, raw..... | 100.00 | 45.45 | 0.205 | 0.101 | 0.306 | 0.152 | 0.458 |
| 1858 | Veal loin, raw..... | 100.00 | 34.87 | 0.293 | 0.131 | 0.424 | 0.168 | 0.592 |
| 1859 | Veal flank, raw..... | 100.00 | 44.34 | 0.258 | 0.049 | 0.307 | 0.174 | 0.481 |
| 1860 | Veal leg, raw..... | 100.00 | 14.44 | 0.453 | 0.150 | 0.603 | 0.246 | 0.849 |
| 1861 | Veal hind shank, raw .. | 100.00 | 18.47 | 0.400 | 0.084 | 0.484 | 0.217 | 0.701 |
| | Average (9)..... | 100.00 | 28.81 | 0.323 | 0.110 | 0.433 | 0.248 | 0.681 |
| 1801 | Beef round, boiled..... | 100.00 | 8.92 | .... | .... | 0.189 | 0.219 | 0.408 |
| 1807 | Beef round, boiled..... | 100.00 | 8.17 | .... | .... | 0.184 | 0.209 | 0.393 |
| 1808 | Beef round, boiled..... | 100.00 | 9.36 | .... | .... | 0.174 | 0.241 | 0.415 |
| 1802 | Beef round, boiled..... | 100.00 | 9.46 | .... | .... | 0.176 | 0.227 | 0.403 |
| 1824 | Beef round, boiled..... | 100.00 | 18.99 | 0.191 | 0.092 | 0.283 | 0.195 | 0.478 |
| 1809 | Beef round, boiled..... | 100.00 | 8.80 | .... | .... | 0.202 | 0.199 | 0.401 |
| 1803 | Beef round, boiled..... | 100.00 | 8.65 | .... | .... | 0.195 | 0.207 | 0.401 |
| | Average (7)..... | 100.00 | 10.34 | .... | .... | 0.200 | 0.214 | 0.414 |
| 1825 | Beef round, pot roast... | 100.00 | 12.58 | 0.275 | 0.133 | 0.408 | 0.187 | 0.595 |
| 1829 | Beef round, pot roast... | 100.00 | 9.80 | 0.261 | 0.114 | 0.375 | 0.154 | 0.529 |
| 1830 | Beef round, pot roast... | 100.00 | 12.35 | 0.268 | 0.046 | 0.314 | 0.265 | 0.580 |
| | Average (3)..... | 100.00 | 11.58 | 0.268 | 0.098 | 0.366 | 0.202 | 0.568 |
| 1831 | Beef rib, roast..... | 100.00 | 66.88 | 0.172 | 0.042 | 0.214 | 0.055 | 0.269 |
| 1833 | Beef rib, roast..... | 100.00 | 61.26 | 0.170 | 0.067 | 0.237 | 0.064 | 0.301 |
| 1837 | Beef rib, roast..... | 100.00 | 53.54 | 0.189 | 0.083 | 0.272 | 0.126 | 0.398 |
| 1838 | Beef rib, roast..... | 100.00 | 54.85 | 0.205 | 0.087 | 0.292 | 0.083 | 0.375 |
| 1840 | Beef rib, roast..... | 100.00 | 63.99 | 0.139 | 0.066 | 0.205 | 0.083 | 0.288 |
| 1842 | Beef rib, roast..... | 100.00 | 64.43 | 0.165 | 0.058 | 0.223 | 0.068 | 0.291 |
| 1844 | Beef rib, roast..... | 100.00 | 59.09 | 0.167 | 0.072 | 0.239 | 0.092 | 0.331 |
| 1846 | Beef rib, roast..... | 100.00 | 50.09 | 0.218 | 0.069 | 0.287 | 0.101 | 0.388 |
| | Average (8)..... | 100.00 | 59.27 | 0.178 | 0.068 | 0.246 | 0.084 | 0.330 |

TABLE IX.—FORMS OF PHOSPHORUS IN MEATS CALCULATED TO WATER- AND FAT-FREE SUBSTANCE.

| Laboratory No. | Kind of meat. | Dry substance (direct). Per cent. | Phosphorus. | | | | |
|---|---|---|---|---|---|---|---|
| | | | Soluble. | | | | |
| | | | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. |
| 1788 | Beef round, raw | 100.00 | 0.516 | 0.177 | 0.693 | 0.214 | 0.907 |
| 1789 | Beef round, raw | 100.00 | 0.453 | 0.196 | 0.649 | 0.284 | 0 933 |
| 1823 | Beef round, raw | 100.00 | 0.404 | 0.436 | 0.840 | 0.157 | 0.997 |
| 1828 | Beef round, raw | 100.00 | 0.455 | 0.214 | 0.669 | 0.267 | 0.936 |
| 1849 | Beef round, raw | 100.00 | 0.621 | 0.424 | 1.045 | 0.260 | 1.305 |
| 1850 | Beef round, raw | 100.00 | 0.665 | 0.451 | 1.116 | 0.382 | 1.499 |
| | Average (6) | 100.00 | 0.519 | 0.316 | 0.835 | 0.261 | 1.096 |
| 1853 | Veal shank, raw | 100.00 | 0.393 | 0.156 | 0.549 | 0.241 | 0.790 |
| 1854 | Veal chuck, raw | 100.00 | 0.400 | 0.167 | 0 568 | 0.324 | 0.892 |
| 1855 | Veal ribs, raw | 100.00 | 0.474 | 0.166 | 0.640 | 0.550 | 1.191 |
| 1856 | Veal shoulder, raw | 100.00 | 0.492 | 0.150 | 0.642 | 0.656 | 1.298 |
| 1857 | Veal breast, raw | 100.00 | 0.375 | 0.185 | 0.560 | 0.280 | 0.840 |
| 1858 | Veal loin, raw | 100.00 | 0.450 | 0.200 | 0.650 | 0.259 | 0.909 |
| 1859 | Veal flank, raw | 100.00 | 0.464 | 0.089 | 0.553 | 0.311 | 0.864 |
| 1860 | Veal leg, raw | 100.00 | 0.530 | 0.175 | 0.705 | 0.287 | 0.992 |
| 1861 | Veal hind shank, raw | 100.00 | 0.491 | 0.103 | 0.594 | 0.266 | 0.860 |
| | Average (9) | 100.00 | 0.452 | 0.155 | 0.607 | 0.353 | 0.960 |
| 1801 | Beef round, boiled | 100.00 | .... | .... | 0.207 | 0.241 | 0.448 |
| 1807 | Beef round, boiled | 100.00 | .... | .... | 0.201 | 0.228 | 0.428 |
| 1808 | Beef round, boiled | 100.00 | .... | .... | 0.192 | 0.266 | 0.458 |
| 1802 | Beef round, boiled | 100.00 | .... | .... | 0.195 | 0.251 | 0.446 |
| 1824 | Beef round, boiled | 100.00 | 0.235 | 0.114 | 0.349 | 0.241 | 0.590 |
| 1809 | Beef round, boiled | 100 00 | .... | .... | 0.221 | 0.219 | 0.440 |
| 1803 | Beef round, boiled | 100.00 | .... | .... | 0.213 | 0.226 | 0.439 |
| | Average (7) | 100.00 | .... | .... | 0.225 | 0.239 | 0.464 |
| 1825 | Beef round, pot roast | 100.00 | 0.315 | 0.152 | 0.467 | 0.214 | 0.681 |
| 1829 | Beef round, pot roast | 100.00 | 0.290 | 0.127 | 0.417 | 0.171 | 0.588 |
| 1830 | Beef round, pot roast | 100.00 | 0.306 | 0.053 | 0.359 | 0.303 | 0.662 |
| | Average (3) | 100.00 | 0.303 | 0.111 | 0.414 | 0.230 | 0.644 |
| 1831 | Beef ribs, roast | 100.00 | 0.521 | 0.126 | 0.647 | 0.164 | 0.811 |
| 1833 | Beef ribs, roast | 100.00 | 0.440 | 0.173 | 0.613 | 0.168 | 0.781 |
| 1837 | Beef ribs, roast | 100.00 | 0.407 | 0.178 | 0.586 | 0.270 | 0.855 |
| 1838 | Beef ribs, roast | 100.00 | 0.455 | 0.192 | 0.647 | 0.183 | 0.830 |
| 1840 | Beef ribs, roast | 100.00 | 0.387 | 0.182 | 0.569 | 0.230 | 0.799 |
| 1842 | Beef ribs, roast | 100.00 | 0.463 | 0.164 | 0.627 | 0.190 | 0.817 |
| 1844 | Beef ribs, roast | 100.00 | 0.407 | 0.176 | 0.583 | 0.227 | 0.810 |
| 1846 | Beef ribs, roast | 100.00 | 0.436 | 0.138 | 0.574 | 0.204 | 0.778 |
| | Average (8) | 100.00 | 0.440 | 0.166 | 0.606 | 0.204 | 0.810 |

in Table VIII, where the results are calculated to the water-free basis, the average amount of fat in the beef round is 10.39 per cent., with a maximum of 13.75 and a minimum of 8.77, while the average result for the veal is 28.81 per cent., varying from 11.91 per cent. in the shank cut, to 45.45 per cent. in the breast cut. However, from the results as calculated to the water and fat-free basis (see Table IX), it can be seen that this difference in the fat content of the beef and veal samples does not account for the greater amount of phosphorus in the flesh of beef.

While the data here presented are not sufficient to warrant a final conclusion, they do tend to indicate definitely that the flesh of beef contains a greater proportion of phosphorus than does the flesh of veal.

Again, in referring to the results given in Table VII, it will be noted that the amounts of phosphorus in the different cuts of veal from the same animal vary decidedly, the maximum being 0.269 per cent. in the shoulder cut and the minimum being 0.168 per cent. in the breast cut. These differences are just as pronounced when the results are calculated to the water-free basis (see Table VIII), the maximum being 0.920 per cent. in the shoulder and the minimum being 0.458 per cent. in the breast. Apparently, from the data presented in this table the amount of fat has but little influence upon the phosphorus content of the veal. The shank cut, for example, has 11.91 per cent. of fat and 0.696 per cent. of phosphorus; the shoulder, 29.26 per cent. of fat and 0.920 per cent. of phosphorus; and the breast, 45.45 per cent. of fat and 0.458 per cent. of phosphorus. In the first and second cases, the percentage of phosphorus varies directly with the fat content, while in the first and third instances the variation is indirect. There seems to be no definite relation between the amount of fat and the quantity of phosphorus found in the several cuts of veal.

By referring again to Table VII, it is apparent that the phosphorus content of the fresh substance of boiled beef round is considerably less than that of uncooked beef round, notwithstanding the fact that there is decidedly less water in the former than in the latter. The total phosphorus occurring in the fresh substance of boiled beef round varies from 0.143 to 0.213 per cent., the average in the seven samples being 0.168 per cent. In these same samples of boiled beef, the total phosphorus soluble

in cold water ranges from 0.067 to 0.126 per cent., averaging 0.082 per cent. The phosphorus in the form of compounds insoluble in cold water, in the fresh substance of boiled beef round varies from 0.076 to 0.094 per cent., the average being 0.086 per cent. Unfortunately in the analysis of the boiled meats, the determinations of the soluble inorganic phosphorus and of the soluble organic phosphorus were not made.

The difference in the amounts of phosphorus contained in uncooked beef and in boiled beef may be seen better from the data given in Tables VIII and IX in which the results of the analyses are calculated to the water-free basis and to the water-free and fat-free substance respectively. Under the former conditions, the average results for the uncooked beef round are as follows: Total phosphorus 0.985, total soluble phosphorus 0.751 and insoluble phosphorus 0.234 per cent. Upon the same basis the average results from the boiled beef round are as follows: Total phosphorus 0.414, total soluble phosphorus 0.200 and the insoluble phosphorus 0.214 per cent. In other words, the dry substance of uncooked beef round contains 2.4 times as much total phosphorus, 3.8 times as much soluble phosphorus and 1.1 times as much insoluble phosphorus as does the dry substance of the same beef round after it has been cooked in hot water by the method known as boiling. The average amounts of fat contained in the uncooked and in the cooked meat are practically the same, so that the results when calculated to the water-free basis and fat-free substance show the same relations to exist between the several forms of phosphorus in the meats as those indicated above for the water-free substance of the same.

The results given in Table VII, show that the total amount of phosphorus contained in the fresh substance of beef round cooked by pot-roasting is slightly less than that which was found in raw beef round; but, on the other hand, it is considerably greater than that contained in boiled beef round. In the fresh substance the average total soluble phosphorus in the pot-roasted beef is markedly lower than it is in raw beef round. This is due mainly to the greater amount of soluble organic phosphorus which occurs in the uncooked meat. In discussing these differences, it will be better to consider the data obtained after calculating the results to the water-free substance (see Table VIII) so that the variations due to the difference in the water content

of the different kinds of meat may be eliminated as far as possible. Upon this basis the average results for the pot-roasted beef round are as follows: Total phosphorus 0.568, total soluble phosphorus 0.366, insoluble phosphorus 0.202, soluble inorganic phosphorus 0.268 per cent., and soluble organic phosphorus 0.098 per cent. Upon the same basis the average results, so far as available for the boiled beef round, are total phosphorus 0.414, total soluble phosphorus 0.200, and insoluble phosphorus 0.214 per cent. The corresponding average results for the uncooked beef round are total phosphorus 0.985, total soluble phosphorus 0.751, insoluble phosphorus 0.234, soluble inorganic phosphorus 0.466, and soluble organic phosphorus 0.285 per cent. Since the average amounts of fat in the three varieties of meat are so nearly similar, the results above given are, practically speaking, strictly comparable with each other. It is thus evident that the dry substance of pot-roasted beef round contains 1.4 times as much total phosphorus, 1.8 times as much total soluble phosphorus, and only 0.9 times as much insoluble phosphorus as does the water-free substance of boiled beef round. Further, it is also plainly evident that the water-free substance of pot-roasted beef round contains only about 0.6 times as much total phosphorus, about 0.5 times as much total soluble phosphorus, a little more than 0.9 times as much insoluble phosphorus, somewhat less than 0.6 times as much soluble inorganic phosphorus, and a little more than 0.3 times as much soluble organic phosphorus as does the dry substance of uncooked beef round.

The analytical data presented in Table VII, also show that the total phosphorus occurring in the fresh substance of roasted beef ribs varies from 0.148 to 0.214 per cent., the average in the nine samples being 0.179 per cent. In these same samples of meat the total phosphorus soluble in cold water forms from 0.118 to 0.158 per cent., averaging 0.134 per cent. The phosphorus existing in the form of compounds insoluble in cold water, in the fresh substance of beef ribs cooked by roasting, varies from 0.030 to 0.059 per cent., the average being 0.045 per cent. The soluble phosphorus in the form of inorganic substances ranges from 0.081 to 0.120 per cent. of the fresh substance of the roasted beef ribs. The average per cent. of phosphorus in this form equals 0.096 per cent. The phosphorus in the form of

soluble organic matter varies from 0.023 to 0.047 per cent., the average being 0.038 per cent.

The averages given above, when calculated to the water-free substance of the roasted meat, give the following results: Total phosphorus 0.330, total soluble phosphorus 0.246, insoluble phosphorus 0.084, soluble inorganic phosphorus 0.178, and soluble organic phosphorus 0.068 per cent. From the data here given it is evident that the dry substance of the roasted beef contains a smaller amount of each of the forms of phosphorus than does the water-free substance of any of the other kinds of flesh here considered. This higher content of fat accounts for the much smaller quantity of phosphorus in its several forms in the water-free substance of the roasted beef ribs. When the results are calculated to the water-free and fat-free basis (see Table IX), the roasted beef ribs contain decidedly more of each of the forms of phosphorus with one exception, namely, the insoluble phosphorus, than does the water and fat-free substance of the pot-roasted beef round and the boiled beef round. On the other hand, the water and fat-free substance of roasted beef ribs contains much less of all of the several forms of phosphorus than does the uncooked lean beef round, when considered upon the same basis.

### DISTRIBUTION OF THE TOTAL PHOSPHORUS IN FLESH.

In order to show plainly the distribution of the total phosphorus content of flesh between the soluble and the insoluble forms and between the inorganic and the organic forms the results of the analyses have been calculated so as to express these different forms of phosphorus in per cents. of the total and total soluble phosphorus respectively. The data so obtained are presented in Table X.

It is apparent from the results given in Table X that from 69.52 to 80.07 per cent. of the total phosphorus occurring in raw beef round exists in compounds which are soluble in water. The phosphorus forming insoluble compounds varies from 19.93 to 30.48 per cent. of the total phosphorus found in the raw beef round. In the six samples of raw beef round here reported the soluble inorganic phosphorus varies from 40.54 to 56.82 per cent. and the soluble organic phosphorus ranges from 19.54 to 38.29 per cent. of the total phosphorus which these

TABLE X.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE PHOSPHORUS, RESPECTIVELY.

| Laboratory No. | Kind of meat. | Total phosphorus. Per cent. | Total soluble phosphorus. Per cent. | Total phosphorus. | | | | | Total soluble phosphorus. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Soluble. | | | | | | | |
| | | | | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
| 1788 | Beef round, raw | 0.220 | 0.168 | 56.82 | 19.54 | 76.36 | 23.64 | 100.00 | 74.41 | 25.59 | 100.00 |
| 1789 | Beef round, raw | 0.210 | 0.146 | 48.57 | 20.95 | 69.52 | 30.48 | 100.00 | 69.86 | 30.14 | 100.00 |
| 1823 | Beef round, raw | 0.222 | 0.187 | 40.54 | 38.29 | 78.83 | 21.17 | 100.00 | 51.43 | 48.57 | 100.00 |
| 1828 | Beef round, raw | 0.210 | 0.150 | 48.57 | 22.86 | 71.43 | 28.57 | 100.00 | 68.00 | 32.00 | 100.00 |
| 1849 | Beef round, raw | 0.311 | 0.249 | 47.59 | 32.48 | 80.07 | 19.93 | 100.00 | 59.44 | 40.56 | 100.00 |
| 1850 | Beef round, raw | 0.345 | 0.257 | 44.35 | 30.14 | 74.49 | 25.51 | 100.00 | 59.54 | 40.46 | 100.00 |
| | Average (6) | 0 253 | 0.193 | 47.74 | 27.38 | 75.12 | 24.88 | 100.00 | 63.78 | 36.22 | 100.00 |
| 1853 | Veal shank, raw | 0.177 | 0.123 | 49.75 | 19.74 | 69.49 | 30.51 | 100.00 | 71.54 | 28.46 | 100.00 |
| 1854 | Veal chuck, raw | 0.193 | 0.123 | 45.12 | 18.63 | 63.75 | 36.25 | 100.00 | 70.73 | 29.27 | 100.00 |
| 1855 | Veal ribs, raw | 0.236 | 0.127 | 39.80 | 14.02 | 53.82 | 46.18 | 100.00 | 74.02 | 25.98 | 100.00 |
| 1856 | Veal shoulder, raw | 0.269 | 0.133 | 37.92 | 11.54 | 49.46 | 50.54 | 100.00 | 76.69 | 23.31 | 100.00 |
| 1857 | Veal breast, raw | 0.168 | 0.112 | 44.65 | 22.02 | 66.67 | 33.33 | 100.00 | 66.96 | 33.04 | 100.00 |
| 1858 | Veal loin, raw | 0.186 | 0.133 | 49.45 | 21.98 | 71.43 | 28.57 | 100.00 | 69.17 | 30.83 | 100.00 |
| 1859 | Veal flank, raw | 0.175 | 0.112 | 53.70 | 10.30 | 64.00 | 36.00 | 100.00 | 83.93 | 16.07 | 100.00 |
| 1860 | Veal leg, raw | 0.221 | 0.157 | 53.43 | 17.64 | 71.07 | 28.93 | 100.00 | 75.16 | 24.84 | 100.00 |
| 1861 | Veal hind shank, raw | 0.191 | 0.132 | 57.07 | 12.04 | 69.11 | 30.93 | 100.00 | 82.58 | 17.42 | 100.00 |
| | Average (9) | 0.202 | 0.128 | 47.88 | 16.43 | 64.31 | 35.69 | 100.00 | 74.53 | 25.47 | 100.00 |
| 1801 | Beef round, boiled | 0.162 | 0.075 | .... | .... | 46.29 | 53.71 | 100.00 | .... | .... | 100.00 |
| 1807 | Beef round, boiled | 0.143 | 0.067 | .... | .... | 46.85 | 53.15 | 100.00 | .... | .... | 100.00 |
| 1808 | Beef round, boiled | 0.162 | 0.068 | .... | .... | 41.98 | 58.02 | 100.00 | .... | .... | 100.00 |

TABLE X.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE PHOSPHORUS, RESPECTIVELY—*Continued.*

| Laboratory No. | Kind of meat. | Total phosphorus. Per cent. | Total soluble phosphorus. Per cent. | Total phosphorus. | | | | | Total soluble phosphorus. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Soluble. | | | | | | | |
| | | | | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
| 1802 | Beef round, boiled..... | 0.167 | 0.073 | .... | .... | 43.71 | 56.29 | 100.00 | .... | .... | 100.00 |
| 1824 | Beef round, boiled..... | 0.213 | 0.126 | 39.91 | 19.24 | 59.15 | 40.85 | 100.00 | 67.46 | 32.54 | 100.00 |
| 1809 | Beef round, boiled..... | 0.161 | 0 081 | .... | .... | 50.31 | 49.69 | 100.00 | .... | .... | 100.00 |
| 1803 | Beef round, boiled..... | 0.167 | 0.081 | .... | .... | 48.50 | 51.50 | 100.00 | .... | .... | 100.00 |
| | Average (7)..... | 0.168 | 0.082 | .... | .... | 48.11 | 51.89 | 100.00 | .... | .... | 100.00 |
| 1825 | Beef round, pot rsast.... | 0.264 | 0.181 | 46.21 | 22.35 | 68.56 | 31.44 | 100.00 | 67.40 | 32.60 | 100.00 |
| 1829 | Beef round, pot roast.... | 0.227 | 0.161 | 49.34 | 21.59 | 70.93 | 29.07 | 100.00 | 69.57 | 30.43 | 100.00 |
| 1830 | Beef round, pot roast.... | 0.225 | 0.122 | 46.21 | 8.00 | 54.22 | 45.78 | 100.00 | 85.25 | 14.75 | 100.00 |
| | Average (3)..... | 0.239 | 0.155 | 47.26 | 17.31 | 64.57 | 35.43 | 100.00 | 74.07 | 25.93 | 100.00 |
| 1831 | Beef ribs, roast..... | 0.148 | 0.118 | 64.19 | 15.54 | 79.73 | 20.27 | 100.00 | 80.51 | 19.49 | 100.00 |
| 1833 | Beef ribs, roast..... | 0.158 | 0.124 | 56.33 | 22.15 | 78.48 | 21.52 | 100.00 | 71.77 | 28.23 | 100.00 |
| 1837 | Beef ribs, roast..... | 0.187 | 0.128 | 47.59 | 20.86 | 68.45 | 31.55 | 100.00 | 69.53 | 30.47 | 100.00 |
| 1838 | Beef ribs, roast..... | 0.190 | 0.148 | 54.74 | 23.15 | 77.89 | 22.11 | 100.00 | 70.27 | 29.7 | 100.00 |
| 1840 | Beef ribs, roast..... | 0.167 | 0.119 | 48.50 | 22.76 | 71.26 | 28.74 | 100.00 | 68.07 | 31.93 | 100.00 |
| 1848 | Beef ribs roast..... | 0.198 | 0.149 | 51.52 | 23.73 | 75.25 | 24.75 | 100.00 | 68.46 | 31.54 | 100.00 |
| 1842 | Beef ribs, roast..... | 0.159 | 0.122 | 56.60 | 20.13 | 76.73 | 23.27 | 100.00 | 73.77 | 26.23 | 100.00 |
| 1844 | Beef ribs, roast..... | 0.193 | 0.139 | 50.26 | 21.76 | 72.02 | 27.98 | 100.00 | 69.78 | 30.22 | 100.00 |
| 1846 | Beef ribs, roast..... | 0.214 | 0.158 | 56.07 | 17.76 | 73.83 | 26.17 | 100.00 | 75.95 | 24.05 | 100.00 |
| | Average (9)..... | 0.179 | 0.134 | 53.98 | 20.87 | 74.85 | 25.15 | 100.00 | 72.01 | 27.99 | 100.00 |

meats contain. The average results for the six samples of raw beef round show that the total phosphorus is distributed as follows: Soluble inorganic 47.74 per cent., soluble organic 27.38 per cent., total soluble 75.12 per cent. and insoluble 24.88 per cent.

The average results for the nine samples of veal show that the total phosphorus in this kind of flesh is distributed as follows: Soluble inorganic 47.88 per cent., soluble organic 16.43 per cent., total soluble 64.31 per cent. and insoluble 35.69 per cent. It is thus apparent that in veal flesh a considerably greater proportion of the total phosphorus exists in the form of insoluble compounds than occurs in this form in beef flesh. The proportion of the total phosphorus in the soluble organic form in the two kinds of flesh is practically the same but there is a marked difference in the proportion of the soluble organic phosphorus.

In the boiled beef round from 41.98 to 59.15 per cent. of the total phosphorus is found in soluble compounds, the average for the seven samples being 48.11 per cent. The phosphorus existing in insoluble compounds ranges from 40.85 to 58.02 per cent. of the total phosphorus found in the boiled beef round, the average being 51.89 per cent. It is obvious from the data given in the above table that there is a remarkable difference in the nature of the phosphorus content of raw beef round and boiled beef round. In the former case 75.12 per cent. of the total phosphorus is soluble and 24.88 per cent. is insoluble in cold water, while in the latter case only 48.11 per cent. of the total phosphorus is soluble and as much as 51.89 per cent. is insoluble in cold water.

The average results for the three samples of beef round cooked by pot-roasting, show that the total phosphorus in beef flesh thus cooked is distributed as follows: Soluble inorganic 47.26 per cent., soluble organic 17.31 per cent., total soluble 64.57 per cent., and insoluble 35.42 per cent.

In the roasted beef ribs from 68.45 to 79.73 per cent. of the total phosphorus occurring in the cooked meat exists in compounds which are soluble in cold water. The phosphorus forming insoluble compounds varies from 20.27 to 31.55 per cent. of the total phosphorus found in the roasted beef ribs. In the nine samples of roasted beef here reported, the soluble inorganic phosphorus varies from 47.59 to 64.19 per cent. and the soluble

organic ranges from 15.54 to 23.73 per cent. of the total phosphorus which these meats contain. The average results for the nine samples of roasted beef ribs show that the total phosphorus is distributed as follows: Soluble inorganic 53.98 per cent., soluble organic 20.87 per cent., total soluble 74.85 per cent., and insoluble 25.15 per cent. It thus seems that the forms of phosphorus in roasted beef resemble somewhat closely those of uncooked beef but differ decidedly from the forms of phosphorus occurring in boiled and pot-roasted meats.

Again, in referring to the results given in Table X, it will be noted that the total soluble phosphorus of the different kinds of flesh is distributed between the organic and the inorganic compounds as follows: Raw beef round, inorganic phosphorus 63.78 per cent., and organic phosphorus 36.22 per cent.; raw veal, inorganic phosphorus 74.53 per cent., and organic phosphorus 25.47 per cent.; pot-roasted beef round, inorganic phosphorus 74.07 per cent. and organic phosphorus 25.93 per cent.; and roasted beef ribs, inorganic phosphorus 72.01 per cent., and organic phosphorus 27.99 per cent.

### RELATION OF THE VARIOUS FORMS OF PHOSPHORUS TO THE TOTAL AND SOLUBLE ASH.

In Table XI, results are given which indicate the relation existing, in the different kinds of flesh, between the several forms of phosphorus and the total and total soluble ash.

A study of the contents of Table XI shows that the forms of phosphorus in raw beef round expressed in percentage of the total ash give the following average data: Soluble inorganic phosphorus 11.11, soluble organic phosphorus 6.55, total soluble phosphorus 17.66, insoluble phosphorus 5.77, and total phosphorus 23.43 per cent. Upon the same basis the average results for the nine samples of raw veal are as follows: Soluble inorganic phosphorus 9.55, soluble organic phosphorus 3.28, total soluble phosphorus 12.83, insoluble phosphorus 7.49, and total phosphorus 20.22 per cent. From these results, it appears that the mineral constituents of veal contain less phosphorus than those of beef. There are also other noticeable differences between the phosphorus content of veal and beef when considered from this standpoint. The total soluble phosphorus in raw beef upon this basis is about 1.4 times as great as it is in the raw veal

TABLE XI.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE ASH, RESPECTIVELY.

| Laboratory No. | Kind of meat. | Total ash. Per cent. | Total soluble ash. cent. | Total phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Total soluble phosphorus. Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 1.090 | 0.874 | 11.47 | 3.94 | 15.41 | 4.77 | 20.18 | 14.30 | 4.92 | 19.22 |
| 1789 | Beef round, raw | 1.060 | 0.947 | 9.62 | 4.15 | 13.77 | 6.04 | 19.81 | 10.77 | 4.65 | 15.42 |
| 1823 | Beef round, raw | 1.080 | 1.002 | 8.33 | 7.87 | 16.20 | 4.36 | 20.56 | 8.98 | 8.48 | 17.46 |
| 1828 | Beef round, raw | 1.060 | 0.940 | 9.62 | 4.53 | 14.15 | 5.66 | 19.81 | 10.85 | 5.11 | 15 96 |
| 1849 | Beef round, raw | 1.110 | 0.988 | 13.46 | 9.18 | 22.64 | 5.63 | 28.27 | 14.98 | 10.22 | 25.20 |
| 1850 | Beef round, raw | 1.080 | 0.991 | 14.17 | 9.63 | 23.80 | 8.14 | 31.94 | 15.44 | 10.49 | 25.93 |
| | Average (6) | 1.080 | 0.960 | 11.11 | 6.55 | 17.66 | 5.77 | 23.43 | 12.55 | 7.32 | 19.87 |
| 1853 | Veal shank, raw | 1.018 | 0.666 | 8.64 | 3.44 | 12.08 | 5.30 | 17.38 | 13.41 | 5.34 | 18.75 |
| 1854 | Veal chuck, raw | 0.995 | 0.667 | 8.74 | 3.62 | 12.36 | 7.04 | 19.40 | 13.04 | 5.40 | 18.44 |
| 1855 | Veal ribs, raw | 0.968 | 0.667 | 9.71 | 3.41 | 13.12 | 11.26 | 24.38 | 14.09 | 4.95 | 19.04 |
| 1856 | Veal shoulder, raw | 1.041 | 0.737 | 9.80 | 2.98 | 12.78 | 13.06 | 25.84 | 13.84 | 4.21 | 18.05 |
| 1857 | Veal breast, raw | 0.897 | 0.655 | 8.36 | 4.13 | 12.49 | 6.25 | 18.67 | 11.45 | 5.65 | 17.10 |
| 1858 | Veal loin, raw | 0.978 | 0.735 | 9.41 | 4.19 | 13.60 | 5.42 | 19.02 | 12.52 | 5.58 | 18.10 |
| 1859 | Veal flank, raw | 0.947 | 0.778 | 9.93 | 1.90 | 11.83 | 6.65 | 18.48 | 12.08 | 2.32 | 14.40 |
| 1860 | Veal leg, raw | 1.094 | 0.887 | 10.79 | 3.56 | 14.35 | 5.85 | 20.20 | 13.30 | 4.40 | 17.70 |
| 1861 | Veal hind shank, raw | 1.029 | 0.761 | 10.59 | 2.24 | 12.83 | 5.73 | 18.56 | 14.32 | 3.03 | 17.35 |
| | Average (9) | 0.996 | 0.727 | 9.55 | 3.28 | 12.83 | 7.39 | 20.22 | 13.12 | 4.54 | 17.66 |
| 1801 | Beef round, boiled | 0.580 | 0.340 | .... | .... | 12.93 | 15.00 | 27.93 | .... | .... | 22.06 |
| 1807 | Beef round, boiled | 0.490 | 0.310 | .... | .... | 13.67 | 15.51 | 29.18 | .... | .... | 21.61 |
| 1808 | Beef round, boiled | 0.560 | 0.420 | .... | .... | 12.14 | 16.79 | 28.93 | .... | .... | 16.19 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1807 | Beef round, boiled | 0.560 | 0.420 | .... | .... | 12.14 | 16.79 | [illegible] | | | | |
| 1808 | Beef round, boiled | 0.560 | 0.420 | .... | .... | | | | | | | |

TABLE XI.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE ASH, RESPECTIVELY—*Continued.*

| Laboratory No. | Kind of meat. | Total ash. Per cent. | Total soluble ash. Per cent. | Total phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Total soluble phosphorus. Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1802 | Beef round, boiled | 0.570 | 0.310 | .... | .... | 12.81 | 16.49 | 29.30 | .... | .... | 23.55 |
| 1824 | Beef round, boiled | 0.830 | 0.620 | 10.24 | 4.94 | 15.18 | 10.82 | 26.00 | 13.71 | 6.61 | 20.32 |
| 1809 | Beef round, boiled | 0.620 | 0.440 | .... | .... | 13.07 | 12.90 | 25.97 | .... | .... | 18.41 |
| 1803 | Beef round, boiled | 0.600 | 0.420 | .... | .... | 13.50 | 14.33 | 27.83 | .... | .... | 19.28 |
| | Average (7) | 0.610 | 0.410 | .... | .... | 13.33 | 14.55 | 27.88 | .... | .... | 20.20 |
| 1825 | Beef round, pot roast | 1.240 | 1.030 | 9.84 | 4.76 | 14.60 | 6.69 | 21.29 | 11.84 | 5.73 | 17.57 |
| 1829 | Beef round, pot roast | 0.950 | 0.680 | 11.79 | 5.16 | 16.95 | 6.95 | 23.90 | 16.47 | 7.21 | 23.68 |
| 1830 | Beef round, pot roast | 0.740 | 0.540 | 14.05 | 2.44 | 16.49 | 13.92 | 30.41 | 19.26 | 3.33 | 22.59 |
| | Average (3) | 0.980 | 0.750 | 11.89 | 4.12 | 16.01 | 9.19 | 25.20 | 15.86 | 5.42 | 21.28 |
| 1831 | Beef rib, roast | 0.830 | 0 650 | 11.45 | 2.77 | 14.22 | 3.61 | 17.83 | 14.62 | 3.53 | 18.15 |
| 1833 | Beef rib, roast | 0.800 | 0.650 | 11.13 | 4.37 | 15.50 | 4.25 | 19.75 | 13.69 | 5.39 | 19.08 |
| 1837 | Beef rib, roast | 0.890 | 0.770 | 10.00 | 4.38 | 14.38 | 6.63 | 21.01 | 11 56 | 5.06 | 16.62 |
| 1838 | Beef rib, roast | 0.900 | 0.710 | 11.55 | 4.89 | 16.44 | 4.67 | 21.11 | 14.65 | 6.20 | 20.85 |
| 1840 | Beef rib, roast | 0.770 | 0.660 | 10.52 | 4.93 | 15.45 | 6.24 | 21.69 | 12.27 | 5.76 | 18.03 |
| 1848 | Beef rib, roast | 1.030 | 0.830 | 9.90 | 4.56 | 14.46 | 4.76 | 19.22 | 12.29 | 5.66 | 17.95 |
| 1842 | Beef rib, roast | 0.880 | 0.670 | 10.23 | 3.63 | 13.86 | 4.20 | 18.07 | 13.43 | 4.78 | 18.21 |
| 1844 | Beef rib, roast | 1.010 | 0.700 | 9.60 | 4.16 | 13.76 | 5.35 | 19.11 | 13.86 | 6.00 | 19.86 |
| 1846 | Beef rib, roast | 1.060 | 0.440 | 11.32 | 3.59 | 14.91 | 5.28 | 20.19 | 27.27 | 8.64 | 35.91 |
| | Average (9) | 0.910 | 0.680 | 10.63 | 4.15 | 14.78 | 5.00 | 19.78 | 14.85 | 5.67 | 20.52 |

while the insoluble phosphorus is somewhat less than 0.8 as much. Further, the amount of phosphorus, in the ash coming from the soluble organic compounds containing phosphorus, is twice as much in the ash from the beef as it is in the ash from the veal.

In the boiled beef round, the total soluble phosphorus equals 13.33 per cent., the insoluble phosphorus equals 14.55 per cent. and the total phosphorus equals 27.88 per cent. of the total ash existing in this kind of flesh. It is thus apparent that the ash of boiled beef, which is much less than the ash of uncooked beef and of veal, contains a somewhat greater proportion of phosphorus than does the ash of raw flesh.

The forms of phosphorus in pot-roasted beef round, in terms of per cent. of the total ash of the same, are as follows: Soluble inorganic phosphorus 11.89, soluble organic phosphorus 4.12, total soluble phosphorus 16.01, insoluble phosphorus 9.19, and total phosphorus 25.20. Upon the same basis, the average results for the nine samples of beef ribs cooked by roasting are as follows: Soluble inorganic phosphorus 10.63, soluble organic phosphorus 4.15, total soluble phosphorus 14.78, insoluble phosphorus 5.00, and total phosphorus 19.78 per cent.

By referring to the results given in Table XI, it will be observed that the total soluble phosphorus in the different kinds of flesh expressed in percentage of the total soluble ash gives the following average results: Raw beef round, inorganic phosphorus 12.55 per cent., organic phosphorus 7.32 per cent., and total phosphorus 19.87 per cent.; raw veal, inorganic phosphorus 13.12 per cent., organic phosphorus 4.54 per cent., and total phosphorus 17.66 per cent.; pot-roasted beef round, inorganic phosphorus 15.86 per cent., organic phosphorus 5.42 per cent., and total phosphorus 21.28 per cent.; roast beef round, inorganic phosphorus 14.85 per cent., organic phosphorus 5.67 per cent., and total phosphorus 20.52 per cent.

### RELATION OF THE PHOSPHORUS AND OF THE NITROGEN IN FLESH TO EACH OTHER.

In order to show the relationship existing between the quantities of the various forms of total phosphorus and of total nitrogen and the various forms of soluble phosphorus and of total soluble nitrogen in the different kinds of flesh, the data given in Table XII are presented. In this table the amount of

phosphorus existing in the different forms is expressed in per cent. of the total nitrogen of the flesh and the quantity of each of the soluble forms of phosphorus is given in percentage of the total soluble nitrogen.

The forms of the total phosphorus in raw beef round expressed in percentage of the total nitrogen of the same are for the average as follows: Soluble inorganic 3.48, soluble organic 2.05, total soluble 5.53, insoluble 1.81, and total phosphorus 7.34. Upon the same basis the average results for the nine samples of raw veal are as follows: Soluble inorganic phosphorus 3.05, soluble organic phosphorus 1.04, total soluble phosphorus 4.09, insoluble phosphorus 2.41, and total phosphorus 6.46 per cent. It is thus apparent that the ratio of soluble inorganic phosphorus to the total nitrogen in raw veal is somewhat less than it is in raw beef and the ratios of the soluble organic phosphorus and of the total soluble phosphorus to total nitrogen in the case of veal are much less than they are in beef flesh. On the other hand, the ratio of the insoluble phosphorus to the total nitrogen is considerably greater in uncooked veal than it is in uncooked beef.

In the boiled beef round the total soluble phosphorus equals 1.44 per cent. of the total nitrogen, the insoluble phosphorus amounts to 1.52 per cent. of the total nitrogen and the total phosphorus forms 2.96 per cent. of the total nitrogen of the flesh.

The forms of the total phosphorus of pot-roasted beef round expressed in percentage of the total nitrogen of the same are as follows: Soluble inorganic 1.95, soluble organic 0.72, total soluble 2.67, insoluble phosphorus 1.47, and total phosphorus 4.14 per cent. Upon the same basis the average results for the nine samples of roasted beef ribs are as follows: Soluble inorganic phosphorus 2.86, soluble organic phosphorus 1.11, total soluble phosphorus 3.97, insoluble phosphorus 1.34 and total phosphorus 5.31 per cent.

The most striking fact brought out by the above figures is the marked difference of the boiled meats from either the meats cooked by other methods or the raw meats. The ratios of the total soluble phosphorus, the insoluble phosphorus and the total phosphorus to the total nitrogen in the boiled flesh are much less than they are in the other cooked or raw meats.

By studying further the results given in Table XII, it will be

TABLE XII.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE NITROGEN, RESPECTIVELY.

| Laboratory No. | Kind of meat. | Total nitrogen. Per cent. | Total soluble nitrogen. Per cent. | Total phosphorus. Soluble. Inorganic. Per cent. | Soluble. Organic. Per cent. | Soluble. Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Total soluble phosphorus. Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1788 | Beef round, raw | 3.6530 | 0.7798 | 3.42 | 1.18 | 4.60 | 1.42 | 6.02 | 16.03 | 5.51 | 21.54 |
| 1789 | Beef round, raw | 3.3650 | 0.7480 | 3.03 | 1.31 | 4.34 | 1.90 | 6.24 | 13.64 | 5.88 | 19.52 |
| 1823 | Beef round, raw | 3.3440 | 0.7885 | 2.69 | 2.54 | 5.23 | 1.41 | 6.64 | 11.41 | 10.77 | 22.18 |
| 1828 | Beef round, raw | 3.3620 | 0.7377 | 3.03 | 1.43 | 4.46 | 1.78 | 6.24 | 13.82 | 6.50 | 20.32 |
| 1849 | Beef round, raw | 3 5450 | 0.8884 | 4.19 | 2.86 | 7.04 | 1.75 | 8.80 | 16.67 | 11.37 | 28.04 |
| 1850 | Beef round, raw | 3.4060 | 0.8998 | 4.49 | 3.05 | 7.54 | 2.58 | 10.12 | 17.00 | 11.55 | 28.55 |
| | Average (6) | 3.4458 | 0.8070 | 3.48 | 2.05 | 5.53 | 1.81 | 7.34 | 14.76 | 8.60 | 23.36 |
| 1853 | Veal shank, raw | 3.3510 | 0.5687 | 2.63 | 1.04 | 3.67 | 1.61 | 5.28 | 15.48 | 6.15 | 21.63 |
| 1854 | Veal chuck, raw | 3.2270 | 0.5536 | 2.70 | 1.11 | 3.81 | 2.17 | 5.98 | 15.72 | 6.50 | 22.22 |
| 1855 | Veal ribs, raw | 2.9340 | 0.5904 | 3.20 | 1.13 | 4.33 | 3.71 | 8.04 | 15.92 | 5.59 | 21.51 |
| 1856 | Veal shoulder, raw | 3.0670 | 0.5988 | 3.32 | 1.01 | 4.33 | 4.43 | 8.77 | 17.05 | 5.17 | 22.21 |
| 1857 | Veal breast, raw | 2.9530 | 0 5367 | 2.54 | 1.25 | 3.79 | 1.90 | 5.69 | 13.97 | 6.90 | 20.80 |
| 1858 | Veal loin, raw | 3.0390 | 0.6001 | 3.03 | 1.35 | 4.38 | 1.74 | 6.12 | 15.33 | 6.83 | 22.16 |
| 1859 | Veal flank, raw | 3.0500 | 0.5889 | 3.13 | 0.60 | 3.73 | .... | 5.82 | 15.96 | 3.06 | 19.02 |
| 1860 | Veal leg, raw | 3.2840 | 0.6790 | 3.59 | 1.19 | 4.78 | 1.95 | 6.73 | 17.38 | 5.74 | 23.12 |
| 1861 | Veal hind shank, raw | 3.3200 | 0.6257 | 3.28 | 0.69 | 3.97 | 1.78 | 5.75 | 17.42 | 3.68 | 21.10 |
| | Average (9) | 3.1361 | 0.5935 | 3.05 | 1.04 | 4.09 | 2.41 | 6.46 | 16.02 | 5.52 | 21.54 |
| 1801 | Beef round, boiled | 5.6860 | 0.1769 | .... | .... | 1.32 | 1.53 | 2.85 | .... | .... | 42.40 |
| 1807 | Beef round, boiled | 5.2490 | 0.1816 | .... | .... | 1.28 | 1.45 | 2.73 | .... | .... | 36.89 |
| 1808 | Beef round, boiled | 5.5550 | 0.2038 | .... | .... | 1.22 | 1.70 | 2.92 | .... | .... | 33.37 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1808 | Beef round, boiled | 5.5550 | 0.2038 | .... | .... | 1.22 | 1.70 | 2.92 | .... | .... | 35.37 |

TABLE XII.—FORMS OF PHOSPHORUS IN MEATS EXPRESSED IN PER CENTS. OF THE TOTAL AND TOTAL SOLUBLE NITROGEN, RESPECTIVELY—*Continued.*

| | | | | Total phosphorus. | | | | | Total soluble phosphorus. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Soluble. | | | | | | | |
| Laboratory No. | Kind of meat. | Total nitrogen. Per cent. | Total soluble nitrogen. Per cent. | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. | Insoluble. Per cent. | Total. Per cent. | Inorganic. Per cent. | Organic. Per cent. | Total. Per cent. |
| 1802 | Beef round, boiled | 5.8860 | 0.1823 | .... | .... | 1.24 | 1.60 | 2.84 | .... | .... | 40.04 |
| 1824 | Beef round, boiled | 5.6110 | 0.3046 | 1.51 | 0.74 | 2.25 | 1.55 | 3.80 | 27.91 | 13.46 | 41.37 |
| 1809 | Beef round, boiled | 5.7420 | 0.3472 | .... | .... | 1.41 | 1.39 | 2.80 | .... | .... | 23.33 |
| 1803 | Beef round, boiled | 5.9630 | 0.2534 | .... | .... | 1.36 | 1.44 | 2.80 | .... | .... | 31.97 |
| | Average (7) | 5.6703 | 0.2357 | .... | .... | 1.44 | 1.52 | 2.96 | .... | .... | 35.62 |
| 1825 | Beef round, pot roast | 5.9690 | 0.4783 | 2.04 | 0.99 | 3.03 | 1.39 | 4.42 | 25.51 | 12.34 | 37.84 |
| 1829 | Beef round, pot roast | 6.0180 | 0.3953 | 1.86 | 0.82 | 2.68 | 1.09 | 3.77 | 28.33 | 12.40 | 40.76 |
| 1830 | Beef round, pot roast | 5.3060 | 0.3365 | 1.96 | 0.34 | 2.30 | 1.94 | 4.24 | 30.91 | 5.35 | 36.26 |
| | Average (3) | 5.7643 | 0.4034 | 1.95 | 0.72 | 2.67 | 1.47 | 4.14 | 28.25 | 10.04 | 38.29 |
| 1831 | Beef ribs, roast | 2.7790 | 0.3300 | 3.42 | 0.83 | 4.25 | 1.08 | 5.33 | 28.79 | 6.97 | 35.76 |
| 1833 | Beef ribs, roast | 3.0600 | 0.3678 | 2.91 | 1.14 | 4.05 | 1.11 | 5.16 | 24.20 | 9.51 | 33.71 |
| 1837 | Beef ribs, roast | 3.3380 | 0.3671 | 2.67 | 1.16 | 3.83 | 1.77 | 5.60 | 24.25 | 10.62 | 34.87 |
| 1838 | Beef ribs, roast | 3.4960 | 0.3520 | 2.97 | 1.26 | 4.23 | 1.20 | 5.43 | 29.55 | 12.50 | 42.05 |
| 1840 | Beef ribs, roast | 3.1960 | 0.3086 | 2.53 | 1.19 | 3.72 | 1.50 | 5.23 | 26.25 | 12.31 | 38.56 |
| 1848 | Beef ribs, roast | 3.8320 | 0.3981 | 2.66 | 1.23 | 3.89 | 1.28 | 5.17 | 25.62 | 11.81 | 37.43 |
| 1842 | Beef ribs, roast | 2.9510 | 0.3207 | 3.05 | 1.08 | 4.13 | 1.26 | 5.39 | 28.06 | 9.98 | 38.04 |
| 1844 | Beef ribs, roast | 3.6310 | 0.3271 | 2.67 | 1.16 | 3.83 | 1.49 | 5.32 | 29.65 | 12.84 | 42.49 |
| 1846 | Beef ribs, roast | 4.1650 | 0.3902 | 2.88 | 0.90 | 3.79 | 1.34 | 5.13 | 30.75 | 9.74 | 40.49 |
| | Average (9) | 3.3853 | 0.3513 | 2.86 | 1.11 | 3.97 | 1.34 | 5.31 | 27.46 | 10.70 | 38.16 |

observed that the different forms of soluble phosphorus expressed in percentage of the total soluble nitrogen give the following average results: Raw beef round, inorganic phosphorus 14.76 per cent., organic phosphorus 8.60 per cent., and total soluble phosphorus 23.36 per cent.; raw veal, inorganic phosphorus 16.02 per cent., organic phosphorus 5.52 per cent., and total soluble phosphorus 21.54 per cent.; pot-roasted beef round, inorganic phosphorus 28.25 per cent., organic phosphorus 10.04 per cent., and total soluble phosphorus 38.29 per cent.; roasted beef ribs, inorganic phosphorus 27.41 per cent., organic phosphorus 10.70 per cent., and total soluble phosphorus 38.16 per cent.

The ratio of the total soluble phosphorus to the total soluble nitrogen is much greater than is the ratio of the total phosphorus to the total nitrogen. This shows very clearly that the total phosphorus existing in flesh is more completely soluble in cold water than is the total nitrogen. Further the ratios of the soluble inorganic phosphorus, the soluble organic phosphorus and the total soluble phosphorus to the total soluble nitrogen are much greater in the three cooked meats than they are in the two raw meats.

NATURE OF THE ORGANIC PHOSPHORUS COMPOUNDS IN FLESH.

Experiments which have been made in this laboratory (see above, page 30) have proved that the soluble proteids of flesh which are coagulated by heat in neutral solutions are practically free from phosphorus. That being the case, the proteid matter precipitated as albumoses from aqueous extracts of flesh by saturation with zinc sulphate was tested for phosphorus. Such tests gave no trace of phosphorus, which shows that the zinc sulphate precipitate contained no phosphorus compounds. In order to test further whether the proteids of cold water extracts contained any phosphorus, portions of such extracts were treated with tannin and salt, which precipitates practically all of the proteids, including albumin, albumoses and peptones. The resulting precipitates were found to be free from phosphorus.

These results prove conclusively that the proteids of aqueous extracts of flesh thus separated do not contain phosphorus but that the organic phosphorus of such solutions is due to non-proteid bodies.

A preliminary study of these non-proteid bodies of flesh which contain phosphorus together with the insoluble phosphorus compounds of flesh has been made but the publication of the results is withheld until they may be further confirmed by additional work.

CONCLUSIONS.

(1) The Hart-Andrews method of separating and determining the inorganic and organic phosphorus gives satisfactory results in aqueous extracts of flesh after the coaguable proteids have been removed.

(2) There is a difference in the phosphorus content of the flesh of beef and veal.

(*a*) Of the total phosphorus in beef 75 per cent. and in veal 64 per cent. is soluble in cold water.

(*b*) Of the total phosphorus, one-fourth is soluble organic phosphorus in the beef and one-sixth in the veal.

(*c*) The soluble organic phosphorus in beef constitutes one-third of the total soluble phosphorus and in the veal one-fourth.

(*d*) The ratio of the soluble organic to the soluble inorganic phosphorus is in the beef, 3:5, and in the veal, 3:9.

(*e*) The phosphorus forms 23.4 per cent. of the ash of beef and 20.2 per cent. of the ash of veal.

(*f*) The soluble forms of phosphorus in beef constitute 17.8 per cent. and in veal 12.8 per cent. of the ash.

(3) The percentage of fat in the different cuts of veal has little influence upon the total phosphorus content.

(4) The cuts of veal which are nearest the bony structure apparently contain more insoluble phosphorus than the other cuts.

(5) The different methods of cooking flesh give products which differ decidedly as to the quantities and the nature of the phosphorus contents.

(6) The water-soluble organic phosphorus of the aqueous extracts of flesh is not in combination with the coagulated proteid, with the albumoses or with the peptones.

(7) The soluble organic phosphorus compounds in flesh are quite stable even in the presence of considerable excess of nitric acid.

# A CHEMICAL STUDY OF SOME OREGON BEAVERDAM SOILS.

By C. E. Bradley.

Received November 22, 1905.

In an effort to work out the fertilizer requirements of some Willamette valley onion soils, a chemical examination of a number of these soils has been made in this laboratory in connection with some field experiments on the same. The results obtained are of interest, since the important features of these most valuable lands are shown.

The beaverdam soils, when virgin, are composed largely of organic material of a peaty nature. The decomposition of leaves, twigs, and fine débris gives rise to one grade, the decay of larger bodies of wood another, while these soils are still further modified by clay washings from surrounding slopes. The term beaverdam is applied to these lands from the fact that beavers were instrumental in forming these swamps by damming the streams which drain them. The vegetation common to these soils is reed-grass, willow, spanish needle, hard-hack, cattails, wild parsnip, etc. The greater portion of these areas overflows in the wet season.

These soils are black when moist, changing to a gray when dry. They are porous, light and loose with no tendency to bake or form lumps. Their characteristic sponginess is shown by a quaking of the earth when loads are driven over them. On account of their large organic content they burn readily when dry, and in consequence of this fact great damage is wrought in these soils by fire. A curious feature is their ability to shed water, due to a resinous content which may be extracted with ether as has been shown. There is no subsoil except at considerable depths.

The following table gives the results of an examination of five of these soils which are typical ones of this class. The crop history and relative productiveness of each is known. The determinations were made by the methods of the Association of Official Agricultural Chemists and the values refer to air-dried samples. The samples were taken to the depth of about twelve inches.

| | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Silica | 20.43 | 51.45 | 36.25 | 21.05 | 53.05 |
| Volatile, loss on ignition | 63.95 | 36.48 | 45.22 | 59.72 | 31.50 |
| Phosphoric acid | 0.26 | 0.31 | 0.22 | 2.30 | 0.21 |
| Potash | 0.14 | 0.28 | 0.13 | 0.10 | 0.20 |
| Soda | 0.17 | 0.16 | 0.20 | 0.27 | 0.43 |
| Lime | 1.09 | 0.26 | 0.47 | 0.92 | 1.18 |
| Magnesia | 0.22 | 0.06 | 0.10 | 0.33 | 0.25 |
| Ferric oxide | 8.29 | 4.00 | 8.40 | 9.21 | 8.03 |
| Alumina | 4.95 | 6.78 | 8.07 | 6.16 | 5.11 |
| Manganese oxide | ..... | ..... | trace | 0.12 | ..... |
| Sulphuric acid | 0.23 | 0.10 | 0.15 | 0.14 | 0.08 |
| | 99.73 | 99.88 | 99.21 | 100.32 | 100.04 |
| Humus | ..... | ..... | 7.72 | 12.75 | 6.56 |
| Potash, 0.5 per cent. HCl | ..... | ..... | 0.022 | 0.052 | 0.010 |
| Potash, J. Law. Smith | ..... | ..... | 0.22 | 0.21 | 0.27 |
| Phosphoric acid, 0.5 per cent. HCl | ..... | ..... | 0.15 | 1.51 | 0.11 |
| Phosphoric acid by HF | ..... | ..... | 0.42 | 2.56 | 0.38 |
| Nitrogen | 1.56 | ..... | 1.81 | 2.06 | 0.78 |
| Organic matter, $CO_2 \times 0.471$ | 42.14 | ..... | ..... | ..... | ..... |

No. 1 is a virgin soil, the others are long farmed. The most productive soils are 3 and 4. Nos. 2, 4 and 5 have had applications of various fertilizers. The field which No. 3 represents has never had an application of any form of fertilizer, but has grown fifty successive crops of onions of good quality and yield. Nos. 2 and 5 have been filled in by washings from sandy soils.

The nitrogen content of these soils is seen to be large, and some application is made of them as nitrogenous fertilizers for clay lands. Potash is present in liberal quantities but is of low availability in the table which corresponds also to the results from field tests, the plants responding quite readily to potash applications. The phosphoric acid is seen to be largely available. The abnormal amount in No. 4 is probably due to the concentration of phosphates in the ash from previous burning of the soil.

The lime content of these soils is sufficient to keep them sweet. Lime is always in excess of magnesia.

The use of 0.5 per cent. HCl for determination of available plant food was suggested by Prof. A. L. Knisely of the Oregon Experiment Station.

PACIFIC UNIVERSITY,
FOREST GROVE, OREGON.

# COMPARATIVE VALUES OF DIFFERENT GRADES OF WHEAT OF CROPS OF 1903 AND 1904.

By R. Harcourt.

Received November 9, 1905.

The exact milling value of each grade of wheat is a question which is arousing a great deal of interest in the Canadian Northwest at the present time. The growers feel that the spread in the price paid for the different grades is wider than it should be, and that the appearance of the grain is taken into consideration more than the actual milling value.

With the object of gaining more definite information regarding the justice of the grading done on individual lots of wheat as delivered by the farmer, the Northwest Territorial Department of Agriculture collected and forwarded to us a number of samples of wheat of the different grades of the crops of 1903 and 1904. A record was kept of the previous cultivation of the ground on which each of the samples was grown. Each sample consisted of approximately eight bushels of wheat. In both years' work, the samples were intended to represent the various grades from No. 1 Hard to No. 4 Northern, in duplicate. Unfortunately, however, when the various lots of wheat were submitted to the Chief Grain Inspector, Winnipeg, for official grading, the grades were changed as shown in Table I.

All the wheat was received in good condition and was from six to eight months old when milled. The milling was done in a short process mill in Guelph. Every means known to the miller was taken to prevent the mixing of the products of the various lots in the milling process and to insure the whole of the products being recovered. The percentage yield of flour given in the following table represents the total yield of flour obtained, but 10 per cent. of low grade was taken from the portion saved for chemical analysis and for the baking tests. The flour was kept in a dry airy room for nearly three months before the analytical and baking work was done. Unfortunately, no record was kept of the weight of 100 grains or of the measured bushels of the various lots of the crop of 1903. The official grading of the samples of both years, the weight of 100 kernels, and weight per measured bushel of the sample for the crop of 1904,

and the percentage yield of flour obtained from the wheat of 1903 and 1904 are given in the following table:

TABLE I.—SHOWING GRADES AND PERCENTAGE YIELD OF FLOUR.

| Grade. | | Weight of 100 kernels. | Weight per measured bus. | Percentage of flour. | |
|---|---|---|---|---|---|
| 1903. | 1904. | 1904. Grams. | 1904. Lbs. | 1903. | 1904. |
| 1 Hard | 1 Hard | 3.2527 | 64.0 | 70.8 | 71.9 |
| 1 " | 1 " | 3.2854 | 64.0 | 69.8 | 72.0 |
| 1 Northern | 1 Northern | 3.2521 | 65.0 | 70.0 | 71.8 |
| 1 " | 1 " | 3.3793 | 65.5 | 69.9 | 72.0 |
| 1 " | 1 " | 3.1531 | 62.5 | 70.7 | 68.3 |
| .... | 1 " | 3.0785 | 61.5 | .... | 69.7 |
| 2 " | .... | .... | .... | 68.3 | .... |
| 3 " | 3 " | 2.9180 | 62.5 | 68.3 | 70.0 |
| 3 " | .... | .... | .... | 68.1 | .... |
| 3 " | .... | .... | .... | 68.2 | .... |
| 4 " | 4 " | 3.1548 | 62.5 | 68.0 | 65.1 |
| .... | 4 " | 2.9194 | 60.0 | .... | 66.1 |

The third sample of No. 1 Northern of the crop of 1903 was what was called "stook frozen" or "riffled" wheat. This wheat was covered with snow while in the stooks. The melting snow apparently softened the wheat and wrinkled it, thus causing it to be graded lower than it otherwise would have been. The two samples of No. 4 Northern of the crop of 1904 were composed almost entirely of Red Fife and would doubtless have graded No. 1 Hard or No. 1 Northern if not frosted. The other samples of the same crop were graded down either because of slight frost or because of the presence of soft grains. One sample was graded as low as No. 5 Northern and has been left out of this report. Millers to whom the samples were shown stated that all the Northern grades were better wheat than they could buy in corresponding grades in Ontario.

In order that the yield of flour obtained by grinding in the large mill might be checked, we sent samples of each lot of wheat of the crop of 1904 to the Columbus Laboratories, Chicago, where they were ground in a small mill especially adapted to determining the yield of flour from comparatively small lots of wheat. The results obtained are embodied in the following table:

TABLE II.—SHOWING WEIGHT PER MEASURED BUSHEL AND YIELD OF FLOUR.

| Grade. | Weight per measured bushel. Uncleaned. Lbs. | Cleaned. Lbs. | Yield of flour from wheat. 100 lbs. uncleaned. | 1 bushel cleaned. | Bushels (60 lbs.) to barrel of flour. Uncleaned. Bus. | Lbs. | Cleaned. Bus. | Lbs. |
|---|---|---|---|---|---|---|---|---|
| 1 Hard | 64 | 65 | 74.2 | 44.5 | 4 | 28 | 4 | 24 |
| 1 " | 64 | 65 | 76 | 45.6 | 4 | 22 | 4 | 18 |
| 1 Northern | 65 | 65 | 74 | 44.4 | 4 | 24.5 | 4 | 24.5 |
| 1 " | 65.5 | 66 | 77.6 | 46.6 | 4 | 14 | 4 | 12 |
| 1 " | 62.5 | 64.5 | 76.3 | 45.8 | 4 | 25 | 4 | 17 |
| 1 " | 61.5 | 63 | 74.9 | 44.9 | 4 | 28 | 4 | 22 |
| 3 " | 62.5 | 63 | 74.3 | 44.6 | 4 | 25.5 | 4 | 23.5 |
| No. 4 | 62.5 | 63 | 73.3 | 44.0 | 4 | 29.5 | 4 | 27 |
| No. 4 | 60 | 61 | 74.5 | 44 7 | 4 | 27 | 4 | 23 |
| No. 5 | 60 | 61 | 72 | 43.2 | 4 | 36 | 4 | 32 |

The figures given in both this and the previous table represent the total yield of flour, as no attempt was made to separate the flour into different grades. It will be noticed that the percentage yield of flour given in Table II is higher than that shown in Table I, but that the variations in yield in one set of figures bear a somewhat similar relationship to those of the other.

It is particularly worthy of notice that while there is a decrease in yield of flour from the lowest grades, there is not that difference which might be expected, considering the wide range in the grading of the wheat. The two samples of No. 4 Northern gave flour slightly darker in color than the others, doubtless due to the fact that it is hard to grind frosted wheat without incorporating some of the wrinkled bran layers. The miller who did the grinding of the large lots stated that the color and yield of the flour from the frosted wheat could have been improved by steaming the wheat before grinding.

No complete chemical analysis was made of either the wheat or the flour, for it was thought that there would not be sufficient difference in the percentage amount of any of the constituents other than proteids to make the analysis of value. The chemical examination was therefore confined to the moisture, proteids and acidity of the flour:

The moisture and acidity were not determined in the flour of the crop of 1903. In the case of the 1904 crop, the moisture determinations were made at the time the other analytical work was done. It will be noticed that the second sample of No. 4 Northern contained a very high percentage of moisture, and,

TABLE III.—SHOWING PERCENTAGE OF MOISTURE, ACIDITY, PROTEIDS, AND GLUTEN.

| Grade. | | Moisture. | Acidity. | Total proteids (N × 5.7). | | Protein soluble in 70 per cent. alcohol (N × 5.7). | | Per cent. of protein soluble in alcohol. | | Gluten, 1903. | | Gluten, 1904. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1903. | 1904. | 1904. | 1904. | 1903. | 1904. | 1903. | 1904. | 1903. | 1904. | Wet. | Dry. | Wet. | Dry. |
| 1 Hard | 1 Hard | 12.48 | 0.26 | 10.9 | 12.2 | 5.77 | 5.84 | 52.8 | 48.1 | 33.2 | 13.3 | 40.8 | 16.3 |
| 1 " | 1 " | 12.98 | 0.12 | 10.8 | 9.3 | 6.32 | 5.15 | 58.3 | 55.4 | 35.0 | 13.8 | 28.7 | 11.1 |
| 1 Northern | 1 Northern | 13.07 | 0.10 | 11.1 | 11.6 | 5.37 | 6.82 | 48.2 | 58.9 | 32.1 | 12.7 | 37.3 | 14.6 |
| 1 " | 1 " | 11.99 | 0.10 | 10.9 | 10.8 | 5.95 | 6.02 | 55.6 | 54.8 | 31.7 | 11.2 | 35.7 | 13.2 |
| 1 " | 1 " | 12.52 | 0.10 | 10.1 | 10.9 | 5.73 | 5.94 | 54.4 | 54.4 | 31.7 | 12.1 | 36.3 | 13.7 |
| .... | 1 " | 12.99 | 0.10 | .... | 10.8 | .... | 5.93 | .... | 54.8 | .... | .... | 34.4 | 13.0 |
| 2 " | .... | .... | .... | 10.7 | .... | 6.08 | .... | 57.1 | .... | 33.8 | 12.8 | .... | .... |
| 3 " | 3 " | 13.07 | 0.08 | 10.7 | 11.4 | 6.20 | 5.64 | 58.2 | 49.3 | 30.5 | 12.2 | 37.1 | 14.7 |
| 3 " | .... | .... | .... | 10.0 | .... | 5.91 | .... | 58.2 | .... | 27.1 | 10.9 | .... | .... |
| 3 " | .... | .... | .... | 10.1 | .... | 6.03 | .... | 58.8 | .... | 31.2 | 12.1 | .... | .... |
| 4 " | 4 " | 13.46 | 0.12 | 11.1 | 11.5 | 6.34 | 6.81 | 57.0 | 59.0 | 33.8 | 13.4 | 36.6 | 13.9 |
| .... | 4 " | 15.83 | 0.28 | .... | 11.7 | .... | 6.61 | .... | 56.3 | .... | .... | 35.4 | 13.6 |

consequently, a high acidity. This flour was quite lumpy two months after it was made. It is quite possible that the wheat was damp when graded and that this fact influenced the Grain Inspector in placing it in a low grade. On the other hand, one sample of No. 1 Hard also contained a high percentage of acidity, and was lumpy, although the percentage of moisture was not high when the determination was made. Unfortunately, no determinations of moisture or acidity were made either in the wheat or flour at the time of grinding.

The percentage amounts of protein in the flour from the various grades of wheat of the 1903 crop are remarkably uniform, the extremes being 9.98 and 11.13. In the 1904 crop the extremes were 9.29 and 12.15. Recently attempts have been made to value wheat for flour purposes by the amount of protein present.[1] It is evident that on this basis of comparison the extremes in quality occur in the two samples of No. 1 Hard of the crop of 1904. According to Prof. Snyder the protein content of a flour is only a general index of bread-making value, and that, provided the proteids do not fall below a certain minimum amount, the composition of the proteid material is of primary importance.[2] Osborne and Voorhees, who have made a special study of the subject, state that gliadin and glutenin are the two principal wheat proteids and that these two substances form the gluten of the flour.[3] Many attempts have been made to determine the ratio that gliadin should bear to glutenin to give the best results for bread-making purposes. The work done in this direction indicates that the gliadin-glutenin ratio varies considerably in wheat grown under similar conditions from year to year, and that these differences have been associated with only minor variations in the size of the loaf or general bread-making value of the flour.[4] Snyder states that "the results available at the present time indicate that the percentage amount of gliadin (or proteids soluble in 70 per cent. alcohol solution) in a flour is of more importance than the gliadin-glutenin ratio."

In view of the foregoing statements regarding the value of the percentage amount of protein and gliadin in forming an idea

[1] A. D. Hall: Journal Board of Agriculture, London, pp. 321–333.
[2] Minn. Agr. Expt. Sta., Bull. 85.
[3] This Journal, 15, 471.
[4] Ibid. 27, 9.

of the value of flour for bread-making purposes, a study of the data presented in Table III reveals the fact that, while there are variations in the amount of protein and gliadin in the various samples of flour, there is no decrease in the quantity which would indicate any falling off in the strength of the flour made from the lower grades of wheat. It is also noticeable that the gluten determinations point to the same conclusion.

For the purpose of obtaining fuller information regarding the nature of the protein content of these different flours, they were analyzed according to the method proposed by J. S. Chamberlain.[1] The results are as follows:

TABLE IV.—SHOWING PER CENT. OF TOTAL NITROGEN AND PER CENT. OF NITROGEN IN FORM OF GLIADIN AND GLUTENIN.

| Grade. | Total nitrogen. | Salt soluble. | Alcohol soluble. | Alcohol insoluble. | Salt soluble of alcohol insoluble. | Glutenin. | Gliadin. | Glutenin. Per cent. | Gliadin. Per cent. |
|---|---|---|---|---|---|---|---|---|---|
| 1 Hard | 2.130 | 0.403 | 1.024 | 1.106 | 0.133 | 0.973 | 0.754 | 56.8 | 43.2 |
| 1 " | 1.630 | 0.376 | 0.903 | 0.727 | 0.112 | 0.615 | 0.639 | 49.0 | 51.0 |
| 1 Northern | 2.025 | 0.399 | 1.197 | 0.828 | 0.091 | 0.737 | 0.889 | 49.4 | 54.6 |
| 1 " | 1.900 | 0.385 | 1.057 | 0.843 | 0.102 | 0.741 | 0.774 | 49.0 | 51.0 |
| 1 " | 1.925 | 0.533 | 1.040 | 0.885 | 0.112 | 0.773 | 0.589 | 56.8 | 43.2 |
| 1 " | 1.900 | 0.483 | 1.041 | 0.859 | 0.134 | 0.725 | 0.692 | 51.1 | 48.9 |
| 3 " | 2.005 | 0.385 | 0.991 | 1.014 | 0.133 | 0.881 | 0.739 | 54.4 | 45.6 |
| 4 " | 2.025 | 0.459 | 1.194 | 0.831 | 0.133 | 0.698 | 0.868 | 44.6 | 55.4 |
| 4 " | 2.060 | 0.329 | 1.159 | 0.901 | 0.137 | 0.764 | 0.967 | 44.2 | 55.8 |

While this proposed method may not make a true separation of the gliadin and glutenin nitrogen, it does give a chance to see something of the gliadin-glutenin ratio. These results do not indicate that the flour from the lower grades of wheat is inferior to that from the wheat which graded very much higher. According to this method of valuation the wheat graded No. 4 Northern would be considered better than that of any of the preceding samples.

To further test the strength of the different flours, they were submitted to actual baking tests. The baking was done by a thoroughly competent man who used all his skill to bring out the best results from each flour. The plan adopted was as follows:

[1] Proceedings of the 20th Annual Convention of the Association of Official Agricultural Chemists.

Six pounds of flour were weighed into a mixing pan and sufficient water, containing the salt and yeast, added to make a dough of medium firmness. Half a pound of flour was weighed into a separate dish to be used as required in making and handling the dough. That portion of the flour not required was weighed back, and from the total weight of flour used the yield of bread was calculated. The doughs were kept throughout at a uniform temperature, and the baking done in a large bake oven. In scoring the bread, the best loaf was credited with 100 points, and the others graded to that. Three bakings were made of each flour. The average yield of bread from each flour and the average score of quality for both years will be found in Table V. The color of the bread was taken into consideration in allotting marks for quality:

TABLE V.—SHOWING YIELD OF BREAD FROM 100 POUNDS OF FLOUR AND THE QUALITY OF THE BREAD.

| Grade. | | Yield of bread per 100 lbs. of flour. | | Quality. | |
|---|---|---|---|---|---|
| 1903. | 1904. | 1903. | 1904. | 1903. | 1904. |
| 1 Hard | 1 Hard | 142.5 | 154.5 | 92.0 | 93.1 |
| 1 " | 1 " | 146.4 | 151.5 | 95.0 | 94.0 |
| 1 Northern | 1 Northern | 146.7 | 153.4 | 95.0 | 94.1 |
| 1 " | 1 " | 144.8 | 153.9 | 92.0 | 96.2 |
| 1 " | 1 " | 140.6 | 155.2 | 95.0 | 96.1 |
| .... | 1 " | .... | 154.8 | .... | 98.0 |
| 2 " | .... | 149.2 | .... | 90.0 | .... |
| 3 " | 3 " | 150.3 | 154.0 | 100.0 | 92.2 |
| 3 " | .... | 146.7 | .... | 95.0 | .... |
| 3 " | .... | 154.0 | .... | 100.0 | .... |
| 4 " | 4 " | 153.3 | 156.8 | 80.0 | 90.2 |
| .... | 4 " | .... | 154.3 | .... | 90.2 |

The bread from the 1904 wheat crop was weighed immediately on being taken from the oven, while that from the 1903 crop was weighed twenty-four hours after coming from the oven. This will account to some extent for the smaller yield of bread from the flour of that year.

In the 1904 samples the quickest working dough was that from the first sample of No. 4 Northern. It also made the largest loaf, while that from the first sample of No. 1 Hard was the smallest. This, it will be noticed, corresponds with the strength of the flour as indicated by the gliadin content.

However, strength in flour is not the only point considered by miller and baker. To satisfy his customers the baker must

produce a white loaf of bread, and, to do this, he must have white flour. As has been stated, the flour from the wheat graded No. 4 Northern was not equal in this respect to that from the higher grades. No figures were obtained that would bring out the differences in color, excepting that it was considered in allotting marks for quality in the bread. In fact, it was the chief cause for the lower marks given to the bread from the lower grades of wheat.

In general, the work here reported indicates that the milling, chemical and baking tests fail to bring out any very wide difference in the products of the individual lots of wheat studied. In yield of flour and in color of the bread the products of the lower grades are inferior, but in strength, as shown by the chemical analysis and in yield of bread, there appears to be little or no difference.

When we take into consideration the fact that the spread in price between No. 1 Hard and No. 4 Northern may amount to twenty-five or even forty cents per bushel, it would appear as though, in this case, the lower grades would not receive the price to which they were entitled, and, consequently, the farmer producing them would not receive justice. On the other hand, it is only fair to state that, according to our system of grading, many other samples graded down for other causes than being frosted may be much inferior in quality and thus reduce the standard of these lower grades. The price, however, is regulated by the quality of the grade as a whole and it may thus happen that individual lots are not paid for in their just merits.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 60.]

## DETERMINATION OF MERCURY AND IODINE IN ANTISEPTIC SOAPS.

BY ATHERTON SEIDELL.

Received November 23, 1905.

THE germicidal character of the halogen salts of mercury has been recognized for a number of years, and comparative experiments, as quoted by Sternberg,[1] have shown that the iodide has

[1] "Text Book of Bacteriology," 1896, p. 188.

more than double the antiseptic value of the bichloride. It has been found by Thomson[1] that mercuric iodide can be introduced into soap without forming an insoluble compound with the fatty acids or losing its antiseptic properties. The mixture is effected by first dissolving the red iodide in a solution of an alkaline iodide and then incorporating it in the melted soap stock. Samples prepared in this manner were found by experiments upon a number of different organisms to be markedly germicidal in their action. More recent experiments along this line appear to have confirmed the observations of Thomson and at present there are a number of mercuric iodide soaps on the market. Rideal, in his book upon "Disinfection and the Preservation of Food," third edition (1903), page 400, states that samples of mercuric iodide soap were found upon analysis to contain 0.37, 0.9 and 3.4 per cents., respectively, of potassium mercuric iodide. Neither the analytical procedure by which these determinations were made nor a reference to it are given by Rideal. Other reference books and a number of journals were examined without success for descriptions of such analyses.

Since no satisfactory method was found by which the mercury and iodine in these soaps could be quantitatively determined, the investigation described in the following pages was undertaken. The plan which first suggested itself was to decompose the fatty material by some suitable means and estimate the mercury and iodine in the residue obtained. Among the methods tried and found unsatisfactory for accomplishing this purpose, were, first, treatment with fuming nitric acid both at the temperature of the steam-bath and in sealed tubes by the method of Carius; second, digestion in a Kjeldahl flask with concentrated sulphuric acid; finally, alternate charring and extraction with acid.

The fatty acids could, of course, be removed from the acidified aqueous solution of the soap by filtration or shaking out with ether, but in either case an unavoidable error would result on account of the solubility of mercuric iodide in the fatty bodies[2]

[1] Thomson: J. Chem. Ind. 7, 192 (1888). The J. Chem. Ind. reports the following patents obtained by Thomson: "An Improved Antiseptic Soap," English Patent No. 9591, July 24, 1886; "Improvements in the Composition of Mercurial Soaps," No. 7117, May 16, 1887. The Chemische Centralblatt reports the German patent, "Preparation of Antiseptic Soaps," D. R. P., No. 49,119, March 22, 1888.

[2] "Solubility of Mercuric Iodide in Fatty Bodies and in Some Other Solvents." Mèhu: J. Pharm. Chim. [5] 12, 249 (1885).

on the one hand and its solubility in the immiscible solvents[1] on the other.

After considering all these points experiments were made as follows, using a sample of soap prepared in the laboratory by mixing a weighed amount of white toilet soap with a solution of mercuric iodide in potassium iodide. Portions of this sample were dissolved in warm water, acidified with hydrochloric acid and, after cooling, an immiscible solvent added to take up the separated fatty acids. Hydrogen sulphide was then passed through the two layers of solution until precipitation appeared complete. The two layers of solution were filtered together and in some cases separately, but in spite of the greatest care a portion of the fatty material would separate from solution and remain on the sides of the Gooch crucible. Great difficulty was experienced in endeavoring to remove this deposit and on this account it became necessary to modify the procedure.

After a number of trials it was finally ascertained that advantage could be taken of the solubility of the fatty acids in strong alcohol, to obtain a homogeneous solution of both the organic and inorganic constituents of the sample. The solution is best obtained by adding to the weighed sample of soap contained in an Erlenmeyer flask about 150 cc. of 95 per cent. alcohol, and 3 to 5 cc. of concentrated hydrochloric acid. The solution is warmed and successive small portions of water added until a perfectly clear solution is obtained on shaking. If suspended particles of impurities are present, the solution should, of course, be filtered. A slow stream of hydrogen sulphide gas is then passed through the liquid for about an hour, after which time the precipitated mercuric sulphide is filtered on a carefully prepared Gooch crucible. The fatty material present in the solution appears to have a tendency to cause the precipitate to pass through the filter, but no trouble on this account need be experienced, if care is taken to use the least amount of suction possible until the sulphide has been washed several times with 95 per cent. alcohol. Although considerable time is required for this filtration, no great delay need be encountered, if a number of determinations are made

[1] "Notice Concerning the Solubility of Mercury Haloid Salts, Especially of Mercuric Iodide in Organic Solvents," Sulc: Z. anorg. Chem. **25**, 399 (1900). "On the Effect of Various Solvents on the Allotropic Change of Mercuric Iodide," Kastle and Clarke: Am. Ch. J. **22**, 473 (1899).

simultaneously. The weight of mercuric sulphide obtained multiplied by 1.955 gives the amount of mercuric iodide in the weight of sample used.

The filtrate and washings from the mercuric sulphide are transferred to a beaker and placed on the steam-bath. When the volume of the solution has been reduced to about one-half or one-third of the original volume, water is added to replace the alcohol, the solution cooled and the separated fats removed by filtration. The clear solution obtained is placed in a glass stoppered separatory funnel together with 25 to 50 cc. of chloroform. The combined iodine is then liberated by the addition of a few drops of nitrous acid. The iodine thus set free is quickly dissolved by the chloroform on shaking, and by repeating the operation two or three times the whole of the iodine is found in the chloroform solution. This latter is then washed by being shaken several times with distilled water. The washings are treated with fresh chloroform to recover any iodine which may have been taken up by them. Finally, the chloroform solution of the iodine is titrated to loss of color with standard sodium thiosulphate solution. The number of cubic centimeters required multiplied by the factor for the standard solution gives the grams of iodine in the sample used.

The nitrous acid solution is prepared by adding to a mixture of about 10 grams of starch and 10 grams of arsenious acid contained in a 700 cc. Erlenmeyer flask about 150 cc. of nitric acid of 1.3 specific gravity. The solution is warmed gently and the reddish $NO+NO_2$ fumes conducted by means of a suitably bent glass tube into a bottle containing about 100 cc. of concentrated sulphuric acid. The solution keeps well and only a few drops are required at a time to liberate the iodine present in the solution under examination.

The method as described above was used for the analysis of several samples of mercuric iodide soap prepared in the laboratory and purchased samples of soap claimed to contain certain amounts of mercuric iodide. The results obtained are shown in the accompanying table.

RESULTS OF THE DETERMINATIONS OF THE MERCURY AND IODINE IN SOAPS CONTAINING MERCURIC IODIDE.

| Sample. | Soap taken. Grams. | $HgI_2$ added or claimed as present. Per cent. | $HgI_2$ found. Per cent. | I (total) found. Per cent. | I as alkali iodide (calculated). Per cent. |
|---|---|---|---|---|---|
| A ..... | 10.0 | 0.83 | 0.92 | 1.00 | 0.48 |
| A ..... | 10.0 | 0.83 | 0.72 | 0.94 | 0.54 |
| A ..... | 10.0 | 0.83 | 0.85 | 1.18 | 0.71 |
| A ..... | 15.0 | 0.83 | 0.96 | 1.07 | 0.54 |
| B ..... | 3.14 | 1.0 | 1.13 | 1.63 | 1.00 |
| C ..... | 3.69 | 1.0 | 0.70 | 0.97 | 0.58 |
| C ..... | 2.87 | 1.0 | 0.78 | 0.90 | 0.46 |
| D ..... | 6.39 | 1.0 | 1.21 | 1.39 | 0.72 |
| D ..... | 8.38 | 1.0 | 0.94 | 1.30 | 0.78 |
| E ..... | 4.33 | 0.1 | 0.11 | 0.17 | 0.11 |
| E ..... | 11.80 | 0.1 | 0.10 | 0.22 | 0.16 |
| E ..... | 3.15 | 0.1 | 0.10 | 0.12 | 0.06 |

Sample A prepared in the laboratory.
B, C and D, different samples of the same brand of soap.
Sample E, a purchased preparation.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 61.]

# A METHOD FOR THE DETERMINATION OF BLACK ALKALI IN IRRIGATING WATERS AND SOIL EXTRACTS.[1]

By W. W. SKINNER.

Received October 28, 1905.

SUCCESSFUL irrigation in an arid region depends to a large extent upon a knowledge of the soluble salts, the so-called alkali, in both soils and the water to be applied to the soils. This is particularly true of black alkali, which is the term applied to certain salts that have a corrosive action upon plants and also have the power of dissolving the humus content of soils. It is from this last characteristic that the prefix black originated, for the humus dissolved by the alkali gives the solution a dark brown or black color, which, when collected in depressions of the soil and evaporated to dryness, produces the very characteristic black alkali spots. Black alkali may therefore be the normal carbonate or bicarbonate of any of the alkalies. As a matter of fact, however, the term has been restricted to mean the carbonate and bicarbonate of sodium. The carbonates of potas-

[1] By permission of the Secretary of Agriculture.

sium and lithium would produce a similar effect to the sodium salts, but are rarely found in sufficient quantities to warrant consideration. The term black alkali is now used by practical irrigators as synonymous with sodium carbonate and it is customary for chemists to express their results in terms of sodium carbonate when soil solutions and irrigating waters are examined for black alkali. As before stated, this is not strictly correct, as small amounts of other salts than soda may be present and estimated as such. Furthermore, the salts may be, and most generally are, present in part at least as bicarbonate. However, when a soil solution containing a bicarbonate is brought to the surface and evaporated to dryness it is quickly changed to the carbonate. The ultimate effect upon plants therefore is the same, whether the sodium salts in the original solution are in the form of carbonate or bicarbonate. The use of the term black alkali, as synonymous with sodium carbonate is believed to be warranted, for all practical purposes.

From what has been before stated it is evident that for a direct determination of the black alkali content of a solution it is necessary to remove the salts of calcium and magnesium. This is effectually accomplished by the method described below, which is a modification and adaptation of the method proposed by Hehner as a substitute for the rather unsatisfactory Clark process for determining the degree of hardness of waters. The modified method has been used by the author in the examination of several hundred samples of irrigating waters and soil extracts and has given uniformly satisfactory results from an analytical standpoint, while the conclusions drawn from the results have been confirmed by actual field observations.

### SOLUTIONS REQUIRED.

(1) A standard N/50 sodium carbonate solution (1 cc. = 0.00106 $Na_2CO_3$).

(2) A standard N/50 sulphuric acid solution (1 cc. is equivalent to 0.0010 $CaCO_3$ or 0.00136 $CaSO_4$).

(3) Indicator, erythrosine (0.25 gram to a liter of water).

(4) Chloroform.

### MANIPULATION.

Two hundred cc. of the water or soil solution to be examined are transferred to a platinum or silver dish, 50 cc. to 150 cc. of

standard sodium carbonate added, the quantity varying with the amounts of soluble salts of calcium and magnesium present, the smaller amount usually being sufficient, and the mixture evaporated to dryness. The residue is rubbed up with distilled water, free from carbon dioxide,[1] transferred to a 100 cc. graduated flask, made up to the mark, thoroughly shaken, stoppered and allowed to stand until clear, which usually requires from twelve to fifteen hours. When clear, 50 cc., equivalent to one-half of the original quantity of water and sodium carbonate added, are carefully removed, without disturbing the residue in bottom of the flask, and transferred to the titrating bottle. For this purpose a bottle of the best white glass without any tinge of pink, with ground glass stopper and of about 250 cc. capacity, is used. Five cc. of chloroform and 1 cc. of the erythrosine solution are added and the solution titrated with the standard acid until the color disappears. The solution should be vigorously shaken after each addition of the acid, the chloroform producing a milky appearance which makes the reading of the end-point sharp and certain.

If less sulphuric acid is required than that necessary to balance one-half of the sodium carbonate added, it is evident that some of the sodium carbonate has been used up, that is, changed by reacting with soluble salts of calcium and magnesium, and is evidence that the solution originally contained no black alkali in excess but rather an excess of the so-called permanent hardness. It is customary to express the hardness in terms of calcium carbonate or calcium sulphate. For irrigation purposes the latter is to be preferred. Therefore the difference in cubic centimeters between the sulphuric acid required and one-half of the sodium carbonate added is multiplied by the factor 0.00136 which gives the equivalent of calcium sulphate in 100 cc. of the water. But if, on the other hand, more sulphuric acid is required than that equivalent to one-half of the sodium carbonate added, then black alkali was originally present in the solution and the difference in cubic centimeters is multiplied by the factor 0.00106, which

[1] For this purpose, distilled water should be vigorously boiled until approximately one-third of the original volume is evaporated, then cooled and stoppered. An ordinary laboratory wash-bottle should not be used to transfer the residue, as the carbon dioxide from the breath of the operator is sufficient to vitiate results.

gives the black alkali in terms of sodium carbonate in 100 cc. of water.

It is necessary in all cases to use an excess of the standard sodium carbonate, as the calcium and magnesium carbonates, which are precipitated in an amorphous form, are quite soluble. The presence of the excess of sodium carbonate decreases their solubility, due to the presence of the common ion $CO_3$.

The method is of peculiar value in the examination of irrigating waters, for not only does it show the character of a water as to black alkali, but if the examination shows a water to contain an excess of the soluble salts of calcium and magnesium, the results are scarcely less valuable, for these soluble salts under proper conditions of irrigation are an antidote for black alkali. Hence, if a soil which already contains black alkali is irrigated with water containing an excess of hardness and proper methods of applying the water are used, favorable results are to be anticipated. The application of this principle was first demonstrated, by Hilgard, with the alkali soils of California, upon which he applied gypsum as an antidote for black alkali.

SUMMARY.

(1) Black alkali is not a definite compound but may consist of the carbonates and bicarbonates of any of the alkalies.

(2) Only the alkalinity due to the carbonates and bicarbonates of the alkalies should be expressed as black alkali, and not the alkalinity due to the carbonates and bicarbonates of the alkaline earths.

(3) While not strictly correct, custom and practical considerations sanction the expression of black alkali in terms of sodium carbonate.

(4) The method described yields satisfactory results for black alkali and also for the antidote for black alkali, *i. e.*, soluble salts of calcium and magnesium, which for irrigation purposes should be expressed in terms of calcium sulphate.

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## A DELIVERY FUNNEL FOR INTRODUCING LIQUIDS UNDER INCREASED OR DIMINISHED PRESSURE.

By T. J. Bryan.

Received October 25, 1905.

The dropping funnel has replaced the thistle tube in cases where a gradual delivery of liquids gives advantage over addi-

tions in quantity. So long as the gases and vapors in the distilling or generating flask have uninterrupted access to the air, there is no difficulty in regulating the delivery to any desired speed by the use of a dropping funnel. At times, however, it becomes necessary (as in cases of the collection or absorption of the gases evolved, or of the protection of the distillate from access of air, etc.) to introduce the use of Woulff bottles, gas washing-bottles, etc., which, as the process of distillation or generation continues, brings about an increase of pressure in the generating flask. This increase of pressure often reaches a point at which it exceeds that produced by the column of liquid in the dropping funnel, and upon opening the stop-cock, not only does the liquid not run down into the flask, but the gases and vapors rise through the funnel, and escape. Attempts to avoid this difficulty, have been made either by filling the tube of the funnel before the operation is commenced,[1] thus increasing the height of the column of liquid; or as is frequently practiced, by inserting this filled tube in a test-tube containing more of the liquid to be delivered. The first method is disadvantageous, especially when the end of the tube is placed in the liquid in the flask, because bubbles of gas or vapor gradually replace the liquid in the tube and necessitate blowing in the top of the funnel or an interruption of the process, to reestablish the desired conditions. The second method, furthermore, is disadvantageous because a quantity of the liquid remains in the test-tube and does not come in contact with the liquid in the flask. Both devices have in all cases the additional disadvantage, that the excess of internal pressure must be less than that of the column of liquid in the funnel.

An apparatus which provides at all times for the same pressure on the upper and lower surfaces of the liquid in the funnel, will evidently solve the above difficulties, for on opening the stop-cock the liquid would then fall by its own weight. Neumann[2] invented an apparatus which intermittently establishes these conditions, and which for some time allows of continuous flow only because of the pressure of a stream of gas delivered into the upper part of the funnel. But Neumann never intended that his apparatus should be used for continuous delivery, for that

[1] Gattermann: "Die Praxis des organischen Chemikers," 1894, p. 156.

[2] J. pr. Chem. [2] 38, 89.

would defeat the very end for which the apparatus was devised, *i. e.*, the introduction of gas into the reaction flask.

It is apparent that a bent tube leading from the flask to the top of the funnel, and properly fitted in rubber stoppers, brings about the desired equality of pressures and admits of either continuous or intermittent delivery from the funnel. The inconvenience of introducing several tubes through one cork; the difficulty of introducing a fresh supply of liquid into the dropping funnel during the reaction with the attendant loss of gases and vapor; and the danger of breaking the apparatus, have led the writer to design the delivery funnel pictured in Fig. 1. It con-

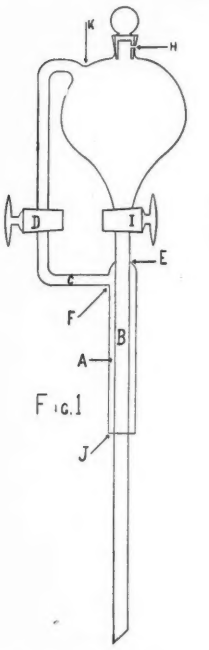

FIG. 1

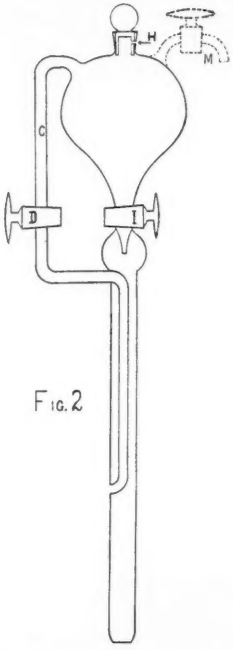

FIG. 2

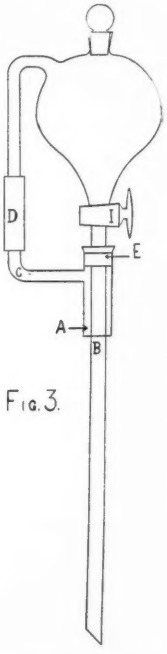

FIG. 3.

sists of a dropping funnel whose tube B passes through and is sealed to the tube A at E. The tube C with a glass stop-cock at D is fused into openings in the upper part of A at F and in the upper part of the funnel at K. The funnel is made with air vent in the stopper.

It is evident from the figure that the working of the apparatus is very simple. The funnel is fitted into the reaction flask by means of a stopper passed over the tube A. When stop-cock I and air vent H are closed, and stop-cock D is open, the same pressure which exists in the reaction flask is exerted through the opening J and the tubes A and C to the upper surface of the liquid in the funnel; and on opening stop-cock I, the same pressure being exerted through B upon the lower surface of the liquid, it flows down through B under a pressure dependent only on the specific gravity of the liquid, the height of its column, and the capillarity of the tube B, which last consideration may be neglected in this connection. The speed of delivery may be regulated by the stop-cock, and the gas pressures on the upper and lower surfaces of the liquid will always remain equal and will allow of either continuous or intermittent delivery so long as a single drop of liquid remains in the funnel. On closing D and I and removing the stopper a fresh supply of liquid may be introduced into the funnel.

In the construction of the apparatus, the lower part of tube B should be of a small bore, for if the capillarity of the opening T in tube A is greater than that of B, a column of liquid formed from condensed vapors is liable to collect in B, somewhat decreasing the pressure in the upper part of the funnel. To further avoid condensation in tube B, its length should be limited to four inches, which gives all the latitude ordinarily desired in regulating the depth to which B shall extend in the flask.

This apparatus though designed by the writer for delivery under increased pressure, is found to be a still greater convenience in working under diminished pressure. In fractional distillation in vacuum, it is frequently desirable to use a very small flask and to distil comparatively large amounts of liquid. If this delivery tube is used, the apparatus may be exhausted while H and I are closed and D is open; it will then be found that on opening I the delivery of the liquid in the funnel can be regulated with the same ease as the flow from an ordinary separatory funnel open at both ends to the air. This quiet delivery instead of the violent spurting which accompanies all attempts to put an ordinary dropping funnel to a similar use, will recommend itself to all who give it a trial. If it is desired, the funnel may be refilled by closing both stop-cocks opening the air vent and removing the stopper. After

filling, it will be necessary to replace the stopper, close the air vent, open the stop-cock D and exhaust before proceeding with the distillation.

Fig. 2 is a modification of Fig. 1 fitted with a Walter's dropping device. The use of the side tube M with its stop-cock, is recommended when it is desirable either to replace air in the apparatus with some other gas, or when it is undesirable to discontinue the distillation in vacuum after refilling the funnel. In the latter case after filling, the funnel and upper part of C are exhausted by attaching a pump to M while D, I and H remain closed; then M is closed, D opened and the conditions are the same as before the flow was interrupted.

A cheaper form of the same apparatus, represented in Fig. 3, gives good results in cases where the reagents used do not attack rubber. This apparatus differs from that in Fig. 1, in that the tubes A and B are joined by means of a rubber stopper instead of being sealed, and the tube C is broken at D and the stop-cock replaced by rubber tubing and a Hofmann's clamp. The length of the tube A is just sufficient to allow its passage through a stopper, thus minimizing the condensation of vapors in A, and the distance that the tube is inserted in the reaction flask is changed by sliding the tube B through the stopper E and adjusting the length of the rubber tube at D. This modification of the delivery tube may be made from a common dropping funnel by any one of ordinary ability at glass-blowing, and is especially adapted to use by students, as the flexibility given by the rubber stopper at E and by the rubber tube at D, reduces the probability of breakage in unskilful hands.

THE UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS, October 23, 1905.

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## SOME OBSERVATIONS ON THE PREPARATION OF METALLIC CALCIUM BY ELECTROLYSIS.

BY S. A. TUCKER AND J. B. WHITNEY.

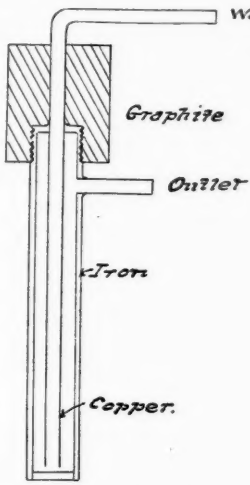
Received October 30, 1905.

THE method for the preparation of this metal used was that devised by J. H. Goodwin,[1] and the attempt was made to improve the yield of the metal if possible.

The apparatus used was similar to that employed by Goodwin,

[1] Proc. Am. Phil. Soc. (Phil.) 43, 381.

and consisted of a graphite crucible turned from an Acheson graphite electrode. This crucible constituted the anode and the




Water cooled Electrode

cavity for the electrolyte was 10 cm. in diameter by 10 cm. deep. The bottom was water-cooled by a coil of copper tube, through which water was circulated, let into the bottom of the crucible. This water-cooling conducts off heat through the thin bottom of graphite, which is made about 3 mm. thick.

A layer of fluorspar is placed upon this, and thus the bottom is protected by a solid crust of the electrolyte during the actual process. At first an iron rod 15 mm. in diameter was used as kathode, as it was desired to test the running of the process on the lines indicated by Goodwin. This kathode was adjustable by means of a wheel and screw mechanism so that it could be elevated or depressed at will.

The raw material for the electrolyte was commercial fused calcium chloride. This is first fused down under the blast-lamp in another crucible, and great care is necessary to insure the absence of any water before introducing it into the anode chamber.

When thoroughly free of water it is poured upon a layer of fluorspar placed on the bottom of this crucible, until the latter

is nearly full. The kathode is immediately lowered and the current turned on.

The heating effect of the current readily melts any of the calcium chloride which may have solidified during the pouring.

When the chloride becomes fluid, calcium immediately begins to collect around the iron kathode, and this is gradually withdrawn in order to get the metal away from the heating influences of the bath as soon as possible, otherwise it is rapidly oxidized.

A number of experiments were made in this way and it was found that with the size of the apparatus given it was only possible to work satisfactorily when the current was kept between the limits of 125 and 150 amperes. With the heavier current the bath became too hot in most cases with consequent loss of calcium by oxidation; if on the other hand the current is allowed to fall to 125 amperes, the metal is deposited in a spongy condition.

It is therefore highly essential that the temperature of the bath be kept constant, and this point should be just below that at which oxidation of the metal begins to take place. Determination of this point by pyrometer measurements gave 720° C. It seemed therefore if the temperature of the kathode could be kept at about 715° C., a better yield of the metal would result.

Regulation by current alone to such fine limits is difficult, and a water-cooled kathode was therefore tried which was found to be successful. The water-cooling was effected by the arrangement here shown, and consists of a piece of gas pipe plugged at one end, and having the water intake near the bottom by means of the bent tube. Another tube takes off the water at the top. The plugging at the bottom should be as thin as possible, as the object is to get the maximum cooling effect to the calcium as it is formed. In this way the metal is cooled almost as it is formed with the result that the yield is much increased. Working with this water-cooled kathode it was found that a yield of 60 per cent. could be obtained.

It is, however, necessary to remove the calcium as it is formed from actual contact with the electrolyte, and this is accomplished by raising the kathode gradually by the hand-wheel; when the rod of calcium thus formed becomes so long that the cooling effect of the water circulation is lost, the metal is removed and

the process again resumed by bringing the cooled iron in contact with the electrolyte.

It is necessary to make this change fairly rapidly, as the temperature of the bath must not be allowed to fall much from that at which the electrolysis takes place. From time to time molten calcium chloride is added to the bath and the process may, in this way, be carried on for a considerable length of time.

Under any circumstances it was found that there was a very considerable loss of the metal due either to oxidation or to recombination of it with the chlorine from the anode. Some experiments were therefore tried with a view to preventing this loss. The kathode was so constructed that the iron rod was surrounded with a graphite bell, the rod being insulated by mica bushings from contact with the graphite. The space inclosed by the bell was about 50 cc. and it was thought probable that the calcium would collect in this space out of contact with the air and away from the influence of the chlorine from the anode. It was found, however, that this arrangement did not give good results, probably from the fact that graphite was used as a material for the bell, as short-circuiting took place soon after it was put in operation. As soon as the bell becomes a conductor it merely acts as a large kathode, decreasing the current density at this point to such a degree that good results are impossible.

COLUMBIA UNIVERSITY.

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## POTASSIUM MERCURIC FERROCYANIDE.

BY GUSTAVE FERNEKES.

Received November 10, 1905.

ON ADDING a solution of potassium ferrocyanide to a solution of mercuric chloride, a yellowish precipitate is at first obtained, which, on standing, turns blue. A qualitative examination of this blue precipitate led me to consider it as potassium mercuric ferrocyanide. On looking into the literature I found no mention of a compound such as I supposed that I had obtained. Kane[1] obtained a compound $K_4Fe(CN)_6+3Hg(CN)_2+4H_2O$ by acting upon a hot solution of mercuric cyanide with potassium ferrocyanide. Loewe[2] obtained the same compound by shaking a moderately concentrated solution of potassium

[1] J. pr. Chem. 19, 405.

[2] Jsb. Chem. 1857, p. 273.

ferricyanide with mercury. Bunsen[1] obtained a salt, $Hg_2Fe(CN)_62NH_3+H_2O$. Pattison-Muir[2] mentions the fact that when a solution of potassium ferrocyanide is added to a solution of a mercuric or mercurous salt, precipitates of unknown composition are obtained.

In the first attempts to isolate the compound aqueous solutions of both mercuric chloride and potassium ferrocyanide were used, but it was found that on adding the ferrocyanide solution to the mercuric chloride solution at room temperature the precipitate formed would run through the filter-paper. When the precipitation is performed at boiling temperature a more flocculent precipitate is obtained, but the decomposition of the compound formed is also more rapid. The precipitation was then tried in hot solutions in an atmosphere of carbon dioxide. With proper precautions and a specially constructed apparatus this would probably have been successful. But at this time it was found that when an aqueous solution of potassium ferrocyanide is added to a solution of mercuric chloride in an equal mixture of alcohol and ether a heavy precipitate is formed which settled very rapidly at room temperature. An attempt was made to replace the aqueous potassium ferrocyanide solution by solid potassium ferrocyanide, but under these conditions the reaction does not take place. When a solution of potassium ferrocyanide is added to a mixture of alcohol and ether not containing any mercuric chloride, the potassium ferrocyanide will be precipitated. Also, if water is added to an alcohol-ether solution of mercuric chloride a precipitate is obtained. Hence, besides the new compound a great quantity of mercuric chloride and potassium ferrocyanide were precipitated. The method finally employed for obtaining the compound was as follows: Fifteen to 20 grams of mercuric chloride were dissolved in about 100 cc. of a mixture of one volume of absolute alcohol to one volume of ether. Eight to 10 grams of potassium ferrocyanide, finely ground, were dissolved in the least possible quantity of water. This latter solution was poured into the mercuric chloride solution and the precipitate allowed to settle. The supernatant alcohol and ether was filtered through a Buchner funnel and a fresh portion of alcohol and ether poured on the precipitate, and

[1] Pogg. Ann. 34, 139.

[2] Watts' Dict., Vol. 2, p. 335.

the flask shaken. Again the alcohol and ether were decanted. Now cold water was poured on the precipitate, which does not settle so rapidly as at first, probably because the greater part of the mercuric chloride had been removed by the alcohol-ether treatment. The whole precipitate was then transferred to the filter-paper and by means of a filter-pump washed within a few minutes with a liter of water cooled to 0° C. It was again carefully washed with alcohol and ether and dried at 100° C. The compound which was obtained was a fine powder with only a very faint blue tinge.

With the substance thus prepared the analysis was made as follows: One-half gram was dissolved in 5 cc. of nitric acid (sp. gr. 1.4) and 2 cc. sulphuric acid (sp. gr. 1.8). It was boiled until white fumes of sulphuric acid were given off. Water was now added and the solution warmed until everything had dissolved. After cooling, the mercury was precipitated as the sulphide and weighed as such on a weighed filter-paper. In the filtrate, after oxidation, the iron was precipitated as hydroxide and weighed as the oxide.

Another portion of 0.5 gram of the substance was analyzed for potassium in the following manner. The decomposition was affected in the same way as mentioned above with the exception that only 1 cc. of sulphuric acid was added. The containing crucible was heated until all the sulphuric acid had been driven off. After the addition of a few cubic centimeters of hydrochloric acid, heat was again applied. The solution was now transferred to a porcelain dish, the mercury and iron removed as before and the resulting solution evaporated to dryness in a weighed platinum dish. After driving off the ammonium chloride, a few drops of sulphuric acid were added and the dish again heated until the excess of sulphuric acid was removed. Finally the temperature was raised until the platinum dish assumed a dull red color. The potassium was thus determined as the sulphate.

For the determination of the cyanogen, 0.5 gram of the compound was decomposed by boiling with 3 grams of yellow mercuric oxide for half an hour. After filtering off the excess of mercuric oxide, and also the iron hydroxide formed, 50 cc. of an ammoniacal zinc sulphate solution were added to the filtrate. A solution of hydrogen sulphide is now added. A black precipitate of mercuric sulphide first comes down. The ammoniacal zinc

sulphate solution serves as an indicator, as zinc only comes down as the sulphide after all the mercury has been precipitated. The end-point then is indicated when, on a fresh addition of hydrogen sulphide solution to the supernatant solution, a pure white precipitate is obtained. The mixture of mercuric and zinc sulphides is now filtered, an excess of silver nitrate added and the solution acidified with nitric acid. The precipitated silver cyanide is filtered, dried, ignited and the silver weighed. From the quantity of silver found the cyanogen is calculated.

The following results, compared with the theoretical percentages of the elements in the compound $K_2HgFe(CN)_6$, agree very closely.

| | Found. Per cent. | Calculated. Per cent. |
|---|---|---|
| Potassium | 15.82 | 15.91 |
| Mercury | 40.63 | 40.61 |
| Iron | 11.45 | 11.40 |
| Cyanogen | 31.78 | 31.81 |
| | 99.68 | 99.73 |

There is therefore no doubt that the above formula must be attributed to the compound. Only a few of the chemical properties of the compound were investigated. With hydrochloric acid the compound becomes blue, with formation of Prussian blue, mercuric chloride and hydroferrocyanic acid. A similar reaction occurs more slowly when the compound is boiled with water. When acted upon by sodium hydroxide, ferric hydroxide, mercuric oxide and potassium ferrocyanide were obtained. The compound is not soluble in water, but a solution of potassium ferrocyanide in water dissolves considerable quantities, probably with formation of a more complex compound. An attempt to isolate a similar compound by acting upon a solution of a mercurous salt with a solution of potassium ferrocyanide has not thus far been successful.

MICHIGAN COLLEGE OF MINES,
November 7, 1905.

# THE RELATION OF THE VOLUME WEIGHT OF RAW CEMENT MATERIAL TO THE OUTPUT OF A ROTARY KILN.

By W. H. Hess.

Received October 20, 1905.

It has been demonstrated in factory practice that rotary kilns of the same size and exactly alike in shape, pitch, speed of rotation and having the same stack dimensions and with the same thickness of fire-brick linings give nearly twice the output in clinker when working on cement rock, or limestone and clay, that they produce when using a mixture of dry marl and clay. The chemical composition of the raw cement materials before calcination is approximately the same in both instances, and the resulting cement has the same chemical and physical properties. While the chemical composition of the marl and clay mixture is practically the same as a cement mixture prepared from limestone and clay, or from cement rock, there is a wide and distinguishing difference among such mixtures in volume weight, so that the chemists may judge of the relative value of limestone chalks, marls, cement rock, or natural cement mixtures, clays, shales, etc., by taking the volume weight of material, prepared by drying and grinding to 100 mesh and mixing in the proper proportions to give the required chemical composition for Portland cement, and comparing data thus acquired with results obtained from testing materials of known efficiency.

By the term "marl" in the above paragraph I refer to the lake deposits of Michigan, Indiana, Canada, etc., which are composed of about 90 per cent. of precipitated chalk, about 5 per cent. of shell lime and 4 to 6 per cent. of organic matter.

*Determination of the Volume Weight.*—Mixtures were prepared from dried samples of marl and clay, chalk and clay, limestone and clay, using the same clay in each instance, and grinding to pass a hundred-mesh sieve. These mixtures were made so that the resulting cement would have the same chemical composition. For the determination a small weighing-bottle of about 25 cc. capacity was used. It was dried and weighed, then filled with distilled water at a temperature of 15° C. and weighed again. The 100-mesh dry powder was then fed into the dried bottle, tapping the bottle carefully on the table to dis-

place all air, and thus packing the bottle full, but no further compression was used, and when the bottle was full and somewhat rounded over the mouth the surface was carefully struck off with a steel spatula, care being taken to avoid any packing of the material. Results obtained by the writer gave for marl alone a weight of 48.7 pounds per cubic foot; for chemically pure precipitated chalk 32.7 pounds per cubic foot; for natural chalk of commerce 70 pounds per cubic foot.

It is evident that considerable variations in results would be obtained, by varying the size and shape of the vessel used for the determination, the method of tapping, etc., but if the chemist will adhere to like conditions throughout a series of tests, comparative results will be obtained.

## EXPERIMENTAL PART.

A series of experimental burnings of cement were made to see if there would be any decided difference in the output of a small rotary kiln, working with different material, and if so, to ascertain the conditions to which such changes in output might be due; and thus develop conclusions from experimental data which might be of value in determining the commercial value of raw cement materials by simple chemical and physical tests.

For this purpose a small rotary was built 14 inches in diameter and 6 feet long, and lined with a 4-inch fire-brick lining, leaving a central opening of 6 inches. It was mounted on trunnions with adjustment for varying the slope, and was driven by an electric motor, the speed of which could be changed as desired. A brick housing was placed at the discharge end, and the escaping kiln gases were carried away by a brick chimney, with a 4- by 8-inch flue. The kiln was fed through an opening at the back of the chimney, the feeding being by hand with a small fire-shovel and sufficiently frequent to spread the material evenly the length of the kiln. Gasoline was used as fuel and was burned under 60 pounds pressure through a large burner specially made in the machine shop, and designed after the Hoskins patent hydrocarbon burner. A 10-gallon riveted steel, cylindrical tank, designated to stand 200 pounds per square inch, was used as a container for the gasoline. It was connected to the burner with a quarter-inch pipe. Pressure was supplied to the gasoline by connecting the tank with an air compressor working under

60 pounds pressure. The container was placed on a set of platform scales so the quantity of fuel consumed could be gauged and recorded. The burner was placed so that the flame passed through a circular 2-inch hole through the housing of the kiln, striking in the center of the kiln flue. With this apparatus about ninety minutes was sufficient to heat the kiln and get good clinker.

Mixtures were prepared of limestone and clay, and Michigan marl and clay, using the same clay for each, and great care was taken to keep the ratio of lime to clay alike in both cases. The analyses of these mixtures were as follows:

| | Limestone and clay. Per cent. | Marl and clay. Per cent. |
|---|---|---|
| Carbonate of lime | 74.80 | 72.20 |
| Carbonate of magnesia | 3.50 | 3.18 |
| Silica | 14.06 | 13.96 |
| Alumina | 5.11 | 4.72 |
| Iron oxide | 2.43 | 2.16 |
| Organic matter, moisture, etc | 0.40 | 3.78 |

Mixtures were also prepared from cement rock, and from chalk and clay, of as nearly the above chemical composition as possible. In each case the mixtures were ground to pass a 100-mesh sieve, then mixed with water to a slurry to insure a thorough amalgamation, and were then dried and reground to 100 mesh powder.

These materials were then burned in the small rotary kiln described above. The same quantity of fuel per unit of time was consumed with each different type of material tested and the same pressure of 60 pounds per square inch was used in each case. The same pitch of rotary and the same rate of rotation was preserved, the only change being in the quantity of material fed per unit of time, this being gauged by the appearance of the cooled clinker, the aim being to obtain dark green clinker with a fixed percentage of brown or underburned clinker, and to feed all the material the kiln would burn without producing more than 10 per cent. of underburned clinker. If the output of underburned clinker was more than 10 per cent. the amount fed was decreased and if the percentage was less than 10 per cent., the feeding was increased, and these changes were kept up until a constant quantity was produced, and the results were then computed into pounds per hour and are given in the following table:

| Material used. | Weight per cu. ft. of fine ground mixture. Lbs. | Weight of raw material consumed. Lbs. | Weight of clinker produced. Lbs. |
|---|---|---|---|
| Marl and clay mixture..... | 52 | 3.8 | 2.2 |
| Limestone clay mixture..... | 88 | 5.8 | 3.5 |
| Cement rock mixture..... | 92 | 6.2 | 3.8 |
| Chalk and clay mixture..... | 70 | 4.8 | 2.8 |

From these results it would appear that the higher the volume weight, or the greater the weight of the ground raw cement mixture per cubic foot, the greater is the output of a kiln, and that the quantity of raw cement material measured in cubic feet, that a kiln will heat to the necessary cement-forming temperature is nearly a constant, all other conditions being the same.

A kiln therefore, using a marl and clay mixture consuming 1125 pounds of coal per hour and producing 1600 pounds cement consumes 2760 pounds cement mixture having a volume of 53 cubic feet. A kiln of the same construction working on a cement rock mixture and consuming 1125 pounds of coal per hour and producing 3200 pounds of cement per hour, burns 52 cubic feet of raw cement mixture per hour. The more dense the raw material, the less space it will occupy in a kiln, and the greater will be the resulting weight of cement which a kiln will produce.

Drying the wet marls of Michigan, Ohio, Indiana, Canada, etc., will not suffice to make them economical materials. Marl is too bulky for a rotary kiln to handle economically; chalk is also too light, and both these materials must in time cease to be a factor in the cement industry. They will gradually be displaced for reasons of economy, and their place will be filled by limestone and cement rock, and even the lighter types of limestone will give way to the heavier class. The higher the specific gravity the better, from an economical point of view.

INDIAN PORTLAND CEMENT CO.,
NEODESHA, KANSAS.

## THE PREPARATION OF 6-BROM-4-KETODIHYDROQUINAZOLINES FROM 5-BROM-2-AMINOBENZOIC ACID AND CERTAIN OF ITS DERIVATIVES.[1]

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received November 22, 1905.

IN A recent paper[2] on the preparation and properties of 5-

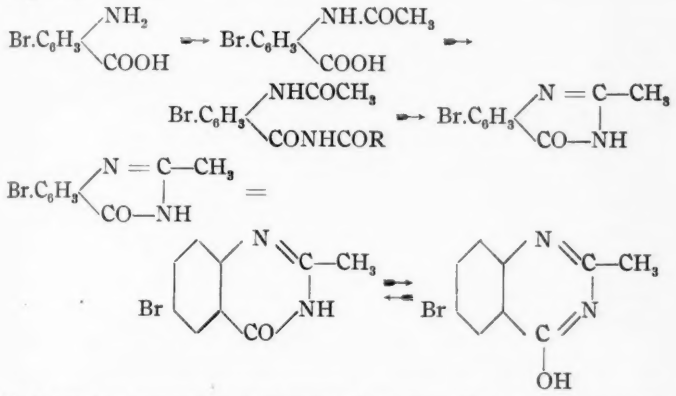
[1] Read at the Buffalo Meeting of the American Chemical Society, June 22, 1905.

[2] This Journal, 27, 1476 (1905).

brom-2-aminobenzoic acid, 5-brom-2-acetaminobenzoic acid, 5-brom-2-acetaminobenzonitrile and 5-brom-2-acetanthranil, we stated that quinazolines had been obtained from these compounds. The present article describes the preparation of these quinazolines.

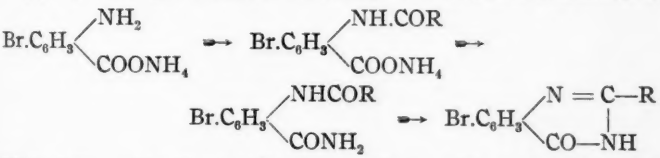
The methods used, although leading to the same or similar final products, varied somewhat with the substance taken as the starting point of the synthesis, and they may be conveniently classified on that basis.

I. *From 5-Brom-2-aminobenzoic Acid.*—(1) By heating the acid in a sealed tube, at 230–250° C., with an acid anhydride and an aliphatic nitrile.[1]



This method proved rather unsatisfactory. Only small amounts can be used; the yield is poor, and the crude product not very pure.

(2) By heating the acid, or its ammonium salt, with acid amides.[2]



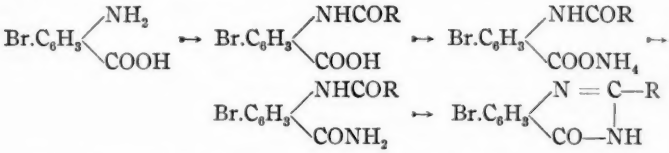
With formamide the results are excellent, with acetamide much less so, while the reaction does not work at all well with the

[1] Bogert and Gotthelf: This Journal, **22**, 129 and 524 (1900); Gotthelf: Ibid. **23**, 611 (1901).

[2] Niementowski: J. pr. Chem. [2] **51**, 564 (1895).

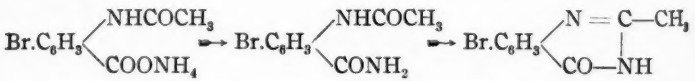
higher amides. This is in accord with Niementowski's own observations.

(3) By heating the acid with excess of glacial formic acid, or an acid anhydride, then adding excess of solid ammonium carbonate and continuing the heating.



This is essentially the same as the next method of preparation, as it probably depends upon the intermediate formation of the acylamino acid. In most cases, it is more convenient to pass thus directly to the quinazolines, without separating and purifying the intermediate acylamino acid. For the best results, the anhydride used should be freshly distilled and in considerable excess (2.5 cc. to 3 cc. of anhydride to 1 gram of the bromanthranilic acid), and, after neutralizing with ammonium carbonate, the heating should be continued for one to three hours. Too long boiling, on the other hand, may impart a yellow color to the product, which is removed only with difficulty. In practically all cases, the iso-anhydrides gave better yields than the normal. With the increase in the molecular weight of the anhydrides, we observed an increasing tendency towards the formation of tarry material insoluble in cold alkali. In the case of the butyric anhydrides, only traces appeared, with isovaleric the amount was greater, while with isocaproic it was still more prominent. If the reaction was carried out properly, the yields were generally good, and the crude products easy to purify.

II. *From 5-Brom-2-acetaminobenzoic Acid by Heating Its Ammonium Salt.*[1]

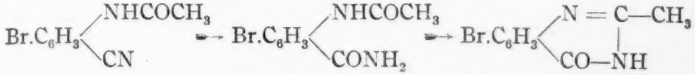


This was carried out only with the acetamino acid, the other acylamino acids not being prepared for the purpose, it being much simpler to prepare the required quinazoline by method

[1] Bischler and Burkart: Ber. 26, 1349 (1893).

I, 3, above. In the case of the acetamino acid, the yield was practically quantitative, but the product was slightly yellow.

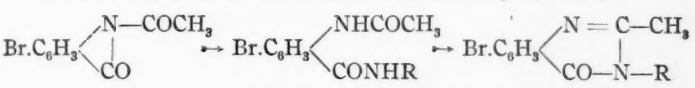
III. *From 5-Brom-2-acetaminobenzonitrile.*—(1) By warming the nitrile with an alkaline dioxide solution.[1]



This is the best process of all, giving immediately a quantitative yield of pure substance.

(2) By boiling the nitrile with concentrated hydrochloric acid. The quinazoline also results when the nitrile is boiled with concentrated hydrochloric acid, the reaction involved being the same as the one just given.

IV. *From 5-Brom-2-acetanthranil and Primary Amines,*[2]



This reaction gives good yields and can be applied to aliphatic or aromatic amines. In fact, as we have had occasion to mention in previous papers, the nitro or halogen acylanthranils appear to condense to quinazoline compounds with almost any primary amino group.

The quinazolines described in this paper, with the exception of those carrying hydrocarbon radicals in position 3 (and which cannot, therefore, rearrange to enolic tautomers), are readily soluble in solutions of the caustic alkalies, but not in ammonia. Carbon dioxide precipitates them from their alkaline solutions. They can be purified conveniently by dissolving them in caustic alkali solution and precipitating by the addition of solid ammonium carbonate to the warm solution. They show but slight affinity for the mineral acids, and these salts when formed are rapidly dissociated by water.

All the melting-points recorded were taken with standardized Anschütz short-scale thermometers. Most of the quinazolines soften slightly before melting. All melting-points were taken by rapid heating, the bath being brought to within a few degrees

[1] Bogert and Hand: This Journal, **24**, 1031 (1902).

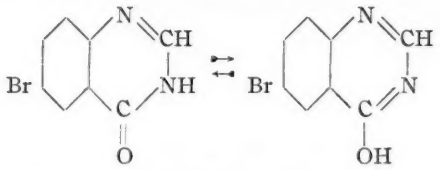
[2] Anschütz, Schmidt and Greiffenberg: Ber. **35**, 3480 (1902); Bogert and Chambers: This Journal, **27**, 649 (1905); Bogert and Seil: Ibid. **27**, 1305 (1905); Bogert and Steiner: Ibid. **27**, 1327 (1905).

of the correct melting-point before the introduction of the melting-point tube.

The necessary analytical work was performed by Messrs. H. J. Smith and J. E. Jacob, of the Chemical Laboratory of the Mississippi Agricultural and Mechanical College, to whom we wish to express our indebtedness for their able assistance.

## EXPERIMENTAL.

*6-Brom-4-ketodihydroquinazoline* (*6-Brom-4-oxyquinazoline*).




(1) *From 5-Brom-2-aminobenzoic Acid and Formamide.*—Ten grams of the bromanthranilic acid were heated with excess of ammonia, the solution evaporated to dryness on the water-bath, and the residue boiled with 15 cc. of formamide until all ammonia was expelled. The contents of the flask were poured into a porcelain dish containing about 100 cc. of hot water, heated on the water-bath, and sufficient 20 per cent. sodium hydroxide solution added to form a clear solution. This solution was filtered hot, and carbonated by adding solid ammonium carbonate to the hot liquid. It was then cooled, filtered, the precipitate washed, treated with bone-black and crystallized from 95 per cent. alcohol. The crystals obtained appeared under the microscope as clear six-sided prisms, and melted at 272–272.5° (corr.) when rapidly heated. The yield of crude product was 9.5 grams.

(2) *From 5-Brom-2-aminobenzoic Acid and Formic Acid.*—Five grams of the bromanthranilic acid were heated with sufficient glacial formic acid to give a clear solution on boiling (14 cc. were used). After boiling for about an hour, excess of solid ammonium carbonate was carefully added, and the temperature then raised to 210–220°, when ammonia was evolved steadily. After heating for fifteen minutes at this temperature, the condensation appeared complete, and the quinazoline was separated and purified as described above, giving rectangular prisms, melting at 272–273° (corr.). The yield of crude product was 1.6 grams.

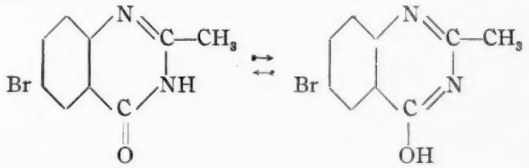
The pure quinazoline forms clear six-sided prisms, m. p. 272–

273° (corr.), when rapidly heated. It is insoluble or difficultly soluble in water, benzene, toluene, cold dilute alcohol, chloroform or carbon tetrachloride; moderately soluble in hot dilute alcohol, cold 95 per cent. alcohol, cold methyl alcohol, cold acetone or cold aniline; easily soluble in the latter solvents at their boiling-points. It crystallizes well from aniline or from dilute alcohol.

Calculated for $C_8H_5ON_2Br$: C, 42.67; H, 2.22; N, 12.44; Br, 35.53. Found: C, 43.03; H, 2.43; N, 12.53; Br, 35.59.

The *chlorplatinate* crystallizes in short, thick prisms. Platinum found, 22.50; calculated, 22.74.

*6-Brom-2-methyl-4-ketodihydroquinazoline* (*6-Brom-2-methyl-4-oxyquinazoline*).



I. *From 5-Brom-2-aminobenzoic Acid.*—(1) By heating the acid in sealed tubes with acetic anhydride and acetonitrile. Three grams of the acid, 3 cc. of acetic anhydride and 3 cc. of acetonitrile were heated together in a sealed tube for five hours at 230–250°. On opening the tube, no pressure was evident. The product was washed out with water, warmed to 60° with a slight excess of sodium hydroxide solution, the solution cooled, filtered, and the quinazoline precipitated from the filtrate with carbon dioxide. The yield was small, and the color of the product golden-yellow, but, on purification, it proved to be identical with the methylquinazoline obtained by the methods described below.

Another tube, charged similarly, but heated six hours at 160–180°, gave a still smaller yield of quinazoline.

(2) By heating the ammonium salt of the acid with acetamide. The dry ammonium salt was intimately mixed with acetamide, and the mixture heated carefully over the free flame until most of the ammonia was driven off. The mass was then boiled up with water, made alkaline with caustic soda, filtered, and the quinazoline precipitated from the filtrate by the addition of solid ammonium carbonate. The precipitate was washed, then treated

with bone-black and recrystallized from alcohol, giving transparent six-sided prisms, m. p. 298–300° (corr.). The yield was only fair.

(3) By treating the acid with acetic anhydride, and then with ammonium carbonate. The acid was boiled for a few minutes with acetic anhydride, then excess of solid ammonium carbonate gradually added to the boiling liquid, and the heating continued until all the ammonia was driven off. The quinazoline was separated as described under '2, and when recrystallized from alcohol was colorless, and identical with that obtained by the other methods. Ten grams of the acid gave 4.3 grams of crude quinazoline.

II. *From 5-Brom-2-acetaminobenzoic Acid by Heating Its Ammonium Salt.*—The acetamino acid was dissolved in excess of ammonia, the solution evaporated to dryness on the water-bath, the dried residue pulverized, and heated in a round-bottomed flask in an oil bath at 220–240° for about an hour. The resultant yellow mass was dissolved in warm dilute caustic soda, the quinazoline precipitated by carbon dioxide, and recrystallized from aniline. The quinazoline obtained was identical with the products described above, except that it was rather more yellow. The crude product was golden-yellow, and it was very difficult to completely remove this color. The yield of crude product was practically quantitative.

There were indications that the reaction began even at 100°, for, after evaporating the ammonium salt to dryness on the water-bath, it continued to smell strongly of ammonia even after prolonged heating at 100°, and the residue was no longer soluble in warm water unless a little ammonia or caustic soda was added.

III. *From 5-Brom-2-acetaminobenzonitrile.*—(1) By the action of sodium dioxide solution upon the nitrile. The nitrile was added to a 5 per cent. aqueous solution of sodium dioxide, warming and stirring until solution was complete. After heating for two hours at 50–70°, the quinazoline was precipitated by a current of carbon dioxide.

Further experience with this method showed that careful heating was not essential, and equally good results were obtained by bringing the solution of the nitrile to a boil, cooling immediately, and precipitating with carbon dioxide. This

method gives a quantitative yield of pure product, and can be readily and rapidly carried out.

(2) By boiling the nitrile with concentrated hydrochloric acid. Attempts to saponify the nitrile by boiling with concentrated hydrochloric acid, instead of giving the desired acid, resulted in a good yield of fairly pure quinazoline.

IV. *From 5-Brom-2-acetanthranil and Ammonia.*—The anthranil was treated with strong ammonia, warmed on the water-bath, the product dissolved in caustic soda, the quinazoline precipitated by solid ammonium carbonate, and purified in the usual way. The yield was excellent.

The products obtained by the various methods outlined above were identical in all respects, and, on analysis, the following figures were secured: C, 45.48; H, 3.35; N, 11.57; Br, 33.49. Calculated for $C_9H_7ON_2Br$: C, 45.19; H, 2.92; N, 11.72; Br, 33.41.

The pure quinazoline separates from dilute alcohol or from aniline in colorless needles, which appear under the microscope as beautiful, clear six-sided prisms. When slowly heated, the compound decomposes, but melts completely at 298–300° (corr.), if plunged in a bath at 295° and rapidly heated.

It is insoluble or difficultly soluble in water, cold dilute ethyl alcohol, cold methyl alcohol, cold acetone, benzene, toluene, cold aniline, chloroform or carbon tetrachloride; moderately soluble in hot dilute ethyl alcohol or hot methyl alcohol; easily soluble in hot acetone or hot aniline. Good crystals may be obtained from either aniline or dilute alcohol. It is readily soluble in dilute solutions of caustic alkalies, and is reprecipitated from such solutions by carbon dioxide or by heating with ammonium carbonate. The compound appears to have but slight affinity for the mineral acids, the hydrochloride, for example, being immediately dissociated by water.

*6-Brom-2-ethyl-4-ketodihydroquinazoline* (*6-Brom-2-ethyl-4-oxyquinazoline*).—Five grams of the bromanthranilic acid and 5 cc. of propionic anhydride were boiled together under a return condenser, an excess of solid ammonium carbonate gradually added to the boiling mass, and the heating continued until the odor of ammonia was no longer noticeable. The quinazoline was separated and purified in the usual way, the yield of crude product being 2.71 grams. On recrystallization, fine needle-like prisms were obtained, melting at 267–268.5° (corr.) when

rapidly heated, with previous softening at 263°, and showing about the same solubilities as the methyl homologue.

Nitrogen found, 11.08; calculated for $C_{10}H_9ON_2Br$, 11.07.

*6-Brom-2-normalpropyl-4-ketodihydroquinazoline* (*6-Brom-2-normalpropyl-4-oxyquinazoline*).—This was prepared in a similar manner, from the bromanthranilic acid and normal butyric anhydride. By using 2.5–3 cc. of freshly distilled anhydride to 1 gram of the bromanthranilic acid, an excellent yield of very pure product was secured. The compound separates from dilute alcohol in needle-like prisms, melting at 255–256° (corr.) when rapidly heated.

Nitrogen found, 10.47; calculated for $C_{11}H_{11}ON_2Br$, 10.49.

*6-Brom-2-isopropyl-4-ketodihydroquinazoline* (*6-Brom-2-isopropyl-4-oxyquinazoline.*—Five grams of the bromanthranilic acid and 9 cc. of isobutyric anhydride were mixed in a round-bottomed flask with return condenser, and boiled gently over the free flame until a clear solution resulted. After boiling for about an hour, an excess of powdered solid ammonium carbonate was gradually added. This caused considerable foaming; in fact, the foaming increases with the rise in the molecular weight of the anhydride used. The temperature of the flask was then raised until a clear melt was again obtained and most of the ammonia driven off. The quinazoline was separated from the melt as already described, and recrystallized from dilute alcohol or from aniline. Any excess of the latter solvent can be removed by washing the crystals with cold carbon tetrachloride, in which the quinazoline is very difficultly soluble. The yield of crude product was 4.2 grams. The pure substance forms colorless needle-like prisms, melting at 259–260.5° (corr.) when rapidly heated. Too long heating, or too high a temperature, in the initial fusion gives a yellowish product.

Nitrogen found, 10.91; calculated for $C_{12}H_{13}ON_2Br$, 10.49.

*6-Brom-2-isobutyl-4-ketodihydroquinazoline* (*6-Brom-2-isobutyl-4-oxyquinazoline*).—Five grams of the bromanthranilic acid and 8 cc. of isovaleric anhydride were heated together for two hours, treated with excess of solid ammonium carbonate, boiled an hour and a half longer, cooled somewhat, boiled up with dilute caustic soda solution, cooled again, filtered, and the quinazoline precipitated in the filtrate with carbon dioxide, as before, giving a yield of 4.7 grams of crude product.

The foaming from the ammonium carbonate was rather troublesome. With the increase in the molecular weight of the anhydride used, there appeared an increasing tendency toward the formation of a tarry body, not soluble in cold alkali, but somewhat soluble in boiling alkali. Traces appeared in the case of the isopropyl derivative, a larger amount in the case of this isobutyl derivative, and still more in the preparation of the following amyl compound. Before filtering the alkaline solution of the quinazoline, therefore, it should be well cooled, as otherwise some of this tar separates from the hot filtrate on cooling.

The pure isobutyl derivative is colorless, and crystallizes in small needle-like prisms, which soften slightly at 250°, and melt with slight decomposition at 253–254° (corr.) when rapidly heated. Like most of these quinazolines, when precipitated by carbon dioxide or by ammonium carbonate, it is very voluminous and difficult to dry thoroughly.

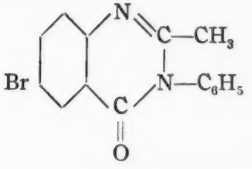
Nitrogen found, 10.32; calculated for $C_{13}H_{15}ON_2Br$, 10.0.

*6-Brom-2-isoamyl-4-ketodihydroquinazoline* (*6-Brom-2-isoamyl-4-oxyquinazoline*).—This was prepared in the same way as the last compound, using 5 grams of the bromanthranilic acid to 11 cc. of isocaproic anhydride. The foaming from the ammonium carbonate was excessive. In the separation of the quinazoline, an appreciable amount of tar remained undissolved by the alkali. This tar was solid at the laboratory temperature, but liquefied on the boiling water-bath. The yield of crude quinazoline was 2.5 grams.

The purified substance crystallizes in needle-like prisms, which melt at 235–236° (corr.) when rapidly heated, and is insoluble or difficultly soluble in water, benzene, toluene, cold aniline, chloroform, carbon tetrachloride, dilute alcohol, cold 95 per cent. alcohol, cold methyl alcohol, or acetone; moderately soluble in hot 95 per cent. alcohol or hot methyl alcohol; easily soluble in hot aniline.

Nitrogen found, 9.80; calculated for $C_{14}H_{17}ON_2Br$, 9.46.

*6-Brom-2-methyl-3-phenyl-4-ketodihydroquinazoline.*



5-Brom-2-acetanthranil was warmed with freshly distilled aniline. The condensation took place smoothly and rapidly. The crude product was treated with bone-black and crystallized from 95 per cent. alcohol, giving colorless six-sided prisms, melting at 185–186° (corr.) when rapidly heated.

Bromine found, 25.9; calculated for $C_{15}H_{11}ON_2Br$, 25.4.

*6-Brom-2-methyl-3-orthotolyl-4-ketodihydroquinazoline.*—This was prepared in similar fashion, from 5-brom-2-acetanthranil and *o*-toluidine. The crude product was dissolved in alcohol, precipitated by the addition of water, the precipitate washed with acetic acid to remove any excess of *o*-toluidine, and recrystallized from dilute alcohol. Colorless crystals were thus obtained, melting at 137–138° (corr.) when rapidly heated.

Bromine found, 24.32; calculated for $C_{16}H_{13}ON_2Br$, 24.30.

In both this case and in the foregoing, the anthranil was carefully washed with carbon tetrachloride before use, to remove any excess of acetic anhydride which might contaminate the product with anilide or toluide.

It will be observed that, with the exception of the methyl derivative, the melting-points of these quinazolines steadily sink with rising molecular weight, and that the iso compounds melt higher than the normal. We have elsewhere called attention to the same condition of affairs in other series of quinazolines.

COLUMBIA UNIVERSITY AND
MISSISSIPPI AGRICULTURAL AND MECHANICAL COLLEGE,
November, 1905.

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CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

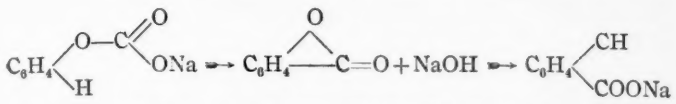
## THE ACTION OF PYRIMIDINE ON SALICYL CHLORIDES.

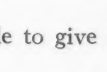
BY RICHARD B. EARLE AND H. LOUIS JACKSON.

Received November 25, 1905.

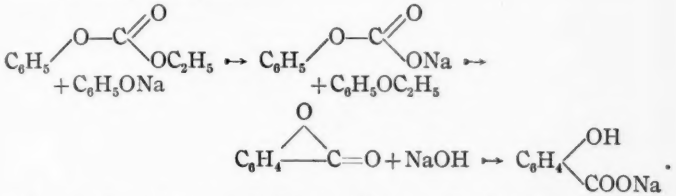
(PRELIMINARY PAPER.)

THE explanation generally given of the reaction involved in the preparation of salicylic acid from sodium phenolate and carbon dioxide is that the sodium phenol carbonate, first formed, rearranges to sodium salicylate. An obvious way of explaining this rearrangement is to assume the formation of an intermediate product, an inner anhydride or lactone of salicylic acid;



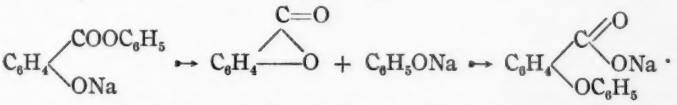
Recently Lobry de Bruyn and S. Tijmstra[1] have brought forward evidence that this view of the formation of salicylic acid is not supported by the facts, and consider that the acid is formed by the direct addition of carbon dioxide to give  , no rearrangement taking place. The arguments, however, do not seem conclusive.

Phenyl ethyl carbonate,[2] if heated with sodium phenolate, reacts readily to form sodium salicylate and phenetol. This also may be considered as a case of the formation of an intermediate body, salicylid,



Attempts have been made by one of us to obtain support for this view by studying the action of sodium and sodium phenolate upon other phenol esters as phenol acetate[3] and benzoate. The results, although interesting, throw no light upon this problem.

A similar rearrangement, which might be explained on the same basis, is that of the sodium salt of salol to the sodium salt of the phenyl ether of salicylic acid,



On account of the possibility that this lactone of salicylic acid may be an intermediate stage in reactions of the sort and also because it would be a $\beta$-lactone, the writers were led to attempt

[1] Rec. trav. chim. Pays-Bas. 23, 385 (1904); Ber. 38, 1375 (1905).

[2] J. pr. Chem. [2] 27, 39 (1883).

[3] Perkin and Hodgkinson: Chem. News, 41, 222 (1880); J. Chem. Soc. 37, 487 (1880).

its isolation in the case of two substituted acids. A large amount of work has already been done in this field, a very brief mention of which follows.

Kraut[1] obtained by heating salicylic acid with acetyl chloride a light yellow resinous mass which he named salicylo-salicylic acid.

Schiff[2] prepared two anhydrides by heating salicylic acid with phosphorus oxychloride, which he called salicylid and tetrasalicylid, and showed that the anhydride gives no color with ferric chloride. He doubted the homogeneity of Kraut's compound.

The action of acetic anhydride on salicylic acid was tried by Perkin.[3] His product was a resinous mass, the physical properties of which were similar to those of the salicylo-salicylic acid of Kraut.

The best work on the subject is that of Anschütz,[4] who obtained two anhydrides which are presumably individuals. These were obtained by heating the acid with phosphorus oxychloride in an indifferent solvent such as toluene or xylene. One of them, which melted at 260–261°, was named by him salicylid, and the other which melted at 322–325°, polysalicylid. Salicylid was found, by its lowering of the freezing-point of phenol to have four times the molecular weight of the true salicylid. A comparison of these anhydrides of Anschütz with those of the earlier investigators establishes the fact that none of the older preparations were at all homogeneous.

F. Hofmann-La Roche and Co.[5] have patented a process for the preparation of salicylid by heating acetylsalicylic acid. Their product possesses a melting-point ranging from 110° C to 210° C. It is probably a mixture. The lack of uniformity of so many of these anhydrides leads to the conclusion that they polymerize on heating.

In all these attempts to prepare salicyl anhydrides the acid is subjected to the action of dehydrating agents with the aid of heat. If, as is probable, they polymerize on heating, such methods do not seem promising. The reaction used in this

[1] Ann. 150, 13 (1869).
[2] Ibid. 163, 218 (1872).
[3] Ber. 16, 339 (1883).
[4] Friedl. Pt., III, 1890–'94, 822.
[5] Friedl. Pt., VI, 1900–'02, 1106.

work seemed hopeful inasmuch as it can be carried out below zero.

The reaction made use of was that of splitting off hydrochloric acid from a substituted salicyl chloride by means of a tertiary base, pyridine being found most convenient. The chloride of salicylic acid itself is not readily made, phosphorus pentachloride acting on the hydroxyl group also, giving compounds containing phosphorus. Anschütz[1] has shown that when salicylic acid contains a substituent ortho to the hydroxyl, it is protected, and phosphorus pentachloride gives the normal acid chloride. The chloride of salicylic acid itself can be made by the action of *p*-toluene sulphone chloride on the acid.[2] However, the easy accessibility of the dichlor and dibrom acid chlorides led us to begin the study of the reaction with them. These chlorides were dissolved in suitable solvents and the calculated amount of pyridine, diluted by the solvent, gradually added.

The results with the dichlor acid chloride were as follows: Benzene was first used as a solvent but its use was given up, as the chief product was a gum from which only a small amount of a substance of a definite melting-point could be obtained. Chloroform gave better results, if used at its boiling-point, the experiments at —10° giving the same sticky gum that was obtained with benzene. This gave about 50 per cent. of the theory of a white amorphous powder, which after recrystallization from nitrobenzene melted with decomposition at about 330° C. It gave no color with ferric chloride. A molecular weight determination was made, using boiling anisol as solvent. As we were unable to find the experimental constant for anisol in the literature, it was determined. The molecular weight found was 734, while that calculated for $(C_6H_2Cl_2OCO)_4$ is 755.6. It is, therefore, a polymer of the substance desired.

The rest of the material dissolved in the chloroform was left on evaporation as a sticky gum which solidified on standing and could be pulverized. Attempts to work with this were unsatisfactory as the substance contained pyridine which we were unable to wash out, it being set free only on decomposition of the substance by boiling alkali solutions, cold solutions of alkali having no effect.

[1] Ber. 30, 221 (1897).

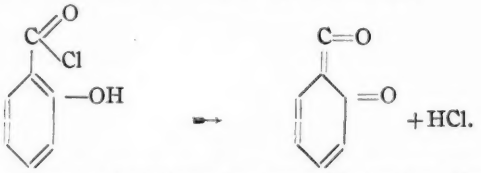
[2] Friedl. Pt., VI, 1900–'02, 35.

The results with the dibrom acid chloride were as follows: As a solvent, petroleum ether at about —10° was first used but it was found that the product contained pyridine from which we were unable to free it. Carbon tetrachloride gave a like result.

The best results were obtained with acetone, cooled to about —10°. The anhydride obtained in this way was found to be free from pyridine, and gave no color with ferric chloride. The melting-point is indeterminate, the substance passing slowly from the solid condition to that of a liquid, over a range of about 100°. Molecular weight determinations indicated it to be heptasalicylid. The behavior on heating indicates, apparently, a lack of homogeneity, but this is not certain.

A very interesting color change was noticed during the action of the pyridine on both of the chlorides. When the pyridine solution is added to that of the chloride, the solution takes on a bright yellow tinge, the color fading quickly, leaving the solution colorless as before. This was the case with all the solvents used, the duration of the color being longest in xylene, in which it lasted for about a minute.

The appearance of this color is so striking and unexpected, that it has led to some speculations as to its cause. It is obviously closely connected with the first stage in the reaction, as its appearance is simultaneous with the addition of the first drops of pyridine solution. One explanation for it consists in the assumption that the first step in the reaction is the breaking off of hydrochloric acid to form an ortho-quinoid body;




Willstätter's[1] recent isolation of quinone diimine has shown that a quinoid grouping of the affinities in the benzene ring does not necessarily imply the presence of color. But the near relationship of this substance to *o*-benzoquinone,[2] a highly colored substance, makes it probable that such a body, if capable of independent existence, would be highly colored.

[1] Ber. 37, 4605 (1904).

[2] Jackson and Koch: Am. Ch. J. 26, 10 (1901).

This explanation of the course of the reaction leads to a clearer understanding of the results obtained. A body of the constitution given would tend to form aggregates containing two or more salicylic acid molecules rather than to form the simpler monosalicylid. The tendency of *o*-benzoquinone to form complex compounds with substances containing hydroxyl groups is well known.[1]

Several attempts to isolate derivatives of this hypothetical substance were made without success. Not enough work has been done yet in this direction to even indicate a suitable method of attack.

## EXPERIMENTAL PART.

*Preparation of 3,5-Dichlorsalicylic Acid.* — Tarugi's[2] method was used at first, but was found to give poor yields of impure substance. The method of Smith[3] gave better results. Fifty grams of salicylic acid were suspended in 250 cc. of glacial acetic acid and a slight excess over the theory of chlorine was passed in, the solution being kept at room temperature by cooling. After an hour's standing the reaction product was filtered off and recrystallized from 90 per cent. acetic acid. About 75 per cent. of the theory was obtained of pure acid, melting at 219.5° C.

*Preparation of 3,5-Dichlorsalicyl Chloride.*[4] — Ten grams of finely powdered dichlorsalicylic acid were heated on the steam-bath in a small flask with 10.2 grams of phosphorus pentachloride. The action is smooth, although it is often necessary to add a slight excess of the chloride to complete the reaction. After an hour's heating on the steam-bath it was diluted with ligroin, cooled to —10° C. and filtered. The white needles thus obtained were found to be practically pure after one crystallization from ligroin. The yield is about 50 per cent. of the theory. Nothing could be gotten from the ligroin mother-liquors but uncrystallizable gums.

Both this and the dibrom acid chlorides are rather unstable; they give off hydrochloric acid slowly on boiling with 60–80° ligroin. Even long standing in a vacuum desiccator causes them to lose hydrochloric acid with the formation of anhydrides.

[1] Am. Ch. J. **26**, 10 (1901).
[2] Gazz. Chim. [2] **30**, 487 (1900).
[3] Ber. **11**, 1225 (1878).
[4] Anschütz: Ber. **30**, 222 (1897).

*The Action of Pyridine on Dichlorsalicyl Chloride.*—Twelve grams of the chloride were dissolved in chloroform, in which it is very easily soluble. Four and three-tenths grams (one molecule) of pyridine, mixed with chloroform, were gradually added. Much heat was developed and the solution turned yellow with each addition of pyridine, the color vanishing almost instantly. The clear reaction mixture was evaporated to a small volume and the gummy mass so obtained washed with benzene. The insoluble matter was washed with water and dried. We obtained thus about 6 grams of a white amorphous powder. It was practically insoluble in all the ordinary solvents, but soluble in boiling nitrobenzene and anisol. It was recrystallized from nitrobenzene, from which it crystallizes in short prismatic crystals, until it melted constant, with decomposition, at about 330° C. It gave no color in alcoholic solution with ferric chloride. It is remarkably stable; boiling with 1 : 1 potassium hydroxide solution dissolves it only slowly, although alcoholic potassium hydroxide hydrolyzes it to the acid in a few seconds. This is obviously due to its extreme insolubility in water.

Analyses by the Dennstedt[1] combustion method gave the following results:

| | Calculated for $C_7H_2O_2Cl_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Carbon | 44.44 | 44.44 | 45.02 |
| Hydrogen | 1.06 | .... | 1.52 |
| Chlorine | 37.57 | 37.34 | 37.67 |

The molecular weight was determined in boiling anisol. The experimental constant of anisol was determined, as it seems not to have been published.

*Boiling-Point Constant of Anisol.*—The anisol used was prepared from phenol and dimethyl sulphate[2] and purified by repeated fractional distillation until the portion taken for the experiment varied only 0.3° C. in boiling-point. The usual Beckmann apparatus was used.

(1) 0.2395 gram of *s*-trinitrobenzene dissolved in 16.16 grams of anisol raised the boiling-point 0.315° C.

(2) 0.5116 gram of *s*-trinitrobenzene dissolved in 16.16 grams of anisol raised the boiling-point 0.663° C.

[1] Ber. 30, 1590, 2861 (1897).

[2] Werner: Ibid. 37, 3658 (1904).

(3) 0.8092 gram of *s*-trinitrobenzene dissolved in 16.16 grams of anisol raised the boiling-point 1.061° C.

| | Calculated for K.[1] | Found. |
|---|---|---|
| 1 | 4595 | 4529 |
| 2 | .... | 4463 |
| 3 | .... | 4515 |
| | | Average = 4502 |

*Molecular Weight of the Anhydride.*—0.6250 gram of substance dissolved in 17 grams of anisol raised the boiling-point 0.225° C.

| Calculated for $(C_6H_2Cl_2OCO)_4$. | Found. |
|---|---|
| 755.6 | 733.6 |

The substance has, therefore, a molecular weight four times that of dichlorsalicylid. It will be noticed that the melting-point is about 70° higher than that of the analogous salicylid of Anschütz, while the difference between the melting-points of the two acids is about 65°.

The remainder of the product of the preceding reaction, obtained by evaporation of the benzene washings, was a colorless gum which gradually solidified to a hard friable mass. It contains, as has so often been the case in this work, pyridine, from which it cannot be freed without decomposition. It is odorless, but develops a strong odor of pyridine on boiling with strong alkalies, although it is scarcely attacked by them in the cold. Work on this substance has proved very puzzling and unsatisfactory, and has been abandoned for the present.

*Preparation of 3,5-Dibromsalicylic Acid.*[2]—Seventy-five grams of salicylic acid were suspended in 375 cc. of glacial acetic acid, and five molecules of bromine added from a burette. The solution was warmed on the steam-bath for several hours, and, after cooling, was filtered from the dibrom acid which separated. This was recrystallized from glacial acetic acid until pure. If, instead of pure acetic acid, the mother-liquors from a previous preparation are used for the bromination, the yield approximates the theory.

*Preparation of Dibromsalicyl Chloride.*—An intimate mixture of dibrom acid and phosphorus pentachloride was warmed in a flask on the steam-bath until the contents were entirely liquid. In most cases it has been found necessary to add an excess of

[1] Longuinine: Ann. chim. phys. [7] 27, 105–144 (1902).

[2] Ber. 17, 2728 (1884).

pentachloride to complete the reaction. The phosphorus oxychloride was distilled off under reduced pressure and the dibrom chloride purified by recrystallization from ligroin until it melted at 83–85° C. The yield was a little over 50 per cent. of the theory.

*Action of Pyridine on the Dibromsalicyl Chloride in Ligroin Solution.*—Twenty-five grams of the chloride were dissolved in a liter of ligroin,[1] and cooled by a freezing-mixture. Six grams of pyridine dissolved in 30 cc. of ligroin were added, drop by drop, the temperature being kept below —6° C. The first drop of pyridine caused the appearance of a yellow precipitate, the color fading immediately. After the precipitate had been filtered off and dried on an unglazed tile it was found to melt at about 77° C.–125° C. The melting-points of the several preparations varied considerably. It gives no color with ferric chloride, but contains pyridine which cannot be removed by treatment with cold alkalies. All attempts to purify it by crystallization or precipitation were failures. The work, however, indicated it to be a mixture.

*The Action of Pyridine on Dibromsalicyl Chloride in Acetone Solution.*—Ten grams of the chloride were dissolved in 140 cc. of acetone, the solution cooled to —16° C. and the calculated amount (2.5 grams) of pyridine diluted with acetone added slowly with constant stirring. The temperature was allowed to rise to —9° C. After standing in the freezing-mixture a short time, the acetone solution was filtered. The precipitate averaged about 50 per cent. of the theory. Dilution of the acetone filtrate with water gave, in some experiments a precipitate, in others a pinkish oil which afterwards solidified. This substance gave a deep purple color with ferric chloride and was, therefore, not further investigated.

The substance which precipitated during the reaction gave no color with ferric chloride and all traces of pyridine were easily washed out with water. We were unable to find any means of purifying it further. On attempting to determine the melting-point it was found that the body passed very slowly from the

[1] It was found in every case that some of the chloride failed to dissolve in the ligroin. This insoluble matter melted at about 170° C. and was evidently an anhydride of some sort. Experiments showed that on boiling the chloride with ligroin, hydrochloric acid was given off, as was easily shown by hanging strips of litmus paper in the condenser. Fifteen minutes' boiling suffices to decompose the chloride to an appreciable extent.

solid to the liquid phase, through a range of about 100°, finally becoming a thick brown liquid at about 223° C.

It is easily soluble in chloroform and benzene, slightly soluble in ether and ethyl acetate, and almost insoluble in ligroin. The act of solution seems to alter the substance, as upon spontaneous evaporation of a benzene or chloroform solution none of the original anhydride could be obtained. One gets instead gummy substances or solids of varying melting-points. It is almost insoluble in ligroin, but ligroin fails to precipitate it from its solutions.

A cryoscopic molecular weight determination in benzene indicated seven molecules in the aggregate, but entire confidence cannot be placed in this because of the possibility that the composition of the substance changes on solution.

As it seemed probable to us that the lack of a definite melting-point might indicate changes in the molecular weight of the substance, a brief study of its behavior on warming was undertaken, with the help of a dilatometer. Two dilatometers containing cotton-seed oil were immersed side by side in an oil-bath provided with a mechanical stirrer. In one of the bulbs the substance was inserted and the bulb sealed. The curve of the oil alone is a straight line from 75–200°. The curve of the substance +oil is a straight line from 75–110° and parallel to that of the oil alone. From 110–170° the substance contracts slowly at a constant rate, while from 170–200° it expands at a rapidly increasing rate. No breaks in the curve were observed.

*Duration of the Color Change.*—A brief comparison of the duration of the yellow color in various solvents is given in the following table:

| | Solvent. | Boiling-point. | Time in seconds. |
|---|---|---|---|
| 1 | Ether | 35.4° | Only a flash of color. |
| 2 | Ethyl acetate | 77° | 0.5 |
| 3 | Acetone | 56.3° | 1 |
| 4 | Ligroin | 50°–60° | 1–2 |
| 5 | Chloroform | 61° | 4 |
| 6 | Mesitylene | 165° | 5 |
| 7 | Carbon tetrachloride | 76° | 30 |
| 8 | Cymene | 175° | 30 |
| 9 | Benzene | 80.4° | 35–40 |
| 10 | Toluene | 110° | 40 |
| 11 | Carbon disulphide | 46° | 45 |
| 12 | Xylene | 142° | 70 |

In this experiment approximately equal amounts of chloride and pyridine were used, without precautions in regard to cooling. As the time of existence of color seemed to increase from benzene to xylene, mesitylene and cymene were used to ascertain whether the progression would continue. This is seen not to be the case.

The addition of various organic bases to the colored solution gave colorless precipitates, some possessing sharp melting-points. Lack of time alone has prevented the investigation of these compounds, which, it is hoped, will be continued this year.

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[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

## ON FISCHER'S CLASSIFICATION OF STEREO-ISOMERS.[1]

BY M. A. ROSANOFF.

Received November 22, 1905.

FISCHER divides optically active substances into two enantiomorphous families. For example, ordinary glucose and levulose (fructose) are classed as members of one family because of their intimate genetic relationship; the two antipodal substances are classed together as members of the opposite family because of a similar relationship. The chemical relationships are indicated by the letters *d* and *l* prefixed to the names of compounds. Thus, ordinary glucose and its corresponding fructose (levulose) are designated, respectively, *d*-glucose and *d*-fructose, notwithstanding the levo-rotation of the latter.

The substances so correlated include, as yet, only the monosaccharides and their derivatives. In other cases the symbols *d* and *l* denote dextro- and levo-rotation. The reform proposed in the following pages, and the importance of avoiding possible confusion, will justify my employing in this paper the Greek $\delta$ and $\lambda$ as family-symbols in place of the customary but misleading *d* and *l*.[2]

The great value of Fischer's classification to systematic stereochemistry is self-evident. The subdivision, however, as established by him in the celebrated memoirs[3] on the configuration of the

[1] Presented before the New York Section of the American Chemical Society on November 10, 1905.

[2] In cases in which misunderstanding is possible, it would be well to prefix the rotation-symbols + or — to the family-symbols, designating ordinary levulose, for instance,—$\delta$-fructose. [On the symbols *d* or *l* might be used, these *l*-$\delta$- fructose. *Editor.*)

[3] Ber. **24**, 1836 and 2683 (1891); Ibid. **27**, 382 and 3208 (1894); etc.

monosaccharides, is inconsistent. Thus, ordinary xylose, which is placed in the *l*-family, changes, not into a *l*-lyxose, as might be expected, but into the lyxose placed in the *d*-family.

The chaos that such inconsistencies are liable to produce is well illustrated by a controversy that ensued some three years ago, when Salkowski and Neuberg[1] succeeded in transforming *d*-glucuronic acid biochemically into *l*-xylose, and interpreted the reaction as the first-known direct transformation of a compound of the *d*-family into one of the *l*-family. Some *d*-compounds are intimately associated in nature with *l*-compounds, and such transformations would show them to be actually biochemical relatives, even though according to Fischer's classification there is no relationship between them and their associated occurrence in nature is apparently accidental. It may be said, however, as Wohl pointed out, that natural xylose was classed by Fischer among the *l*-compounds because its genetic relationship to *l*-gulose happened to have been discovered before its formation from *d*-lyxose was known: had accident (!) reversed the order of discovery, the xylose would have taken a place among the sugars of the *d*-family.[2] Whatever, then, the possibilities of Salkowski and Neuberg's method as such, the theoretical value of the transformation actually effected appeared capable of two very different, yet equally justifiable, estimates. In the same connection, Fischer's classification was examined by W. Küster,[3] who arrived at the conclusion that the designation of natural xylose as a relative of the artificial *l*-glucose is entirely conventional, arbitrary, and that a perfectly consistent classification of the sugars and their derivatives is impossible. Again, the impossibility of a consistent classification is asserted by Salkowski and Neuberg in their reply to Küster's criticism.[4]

A careful re-examination of the subject has led me to a different view, and I propose to show in the present paper that while Fischer's subdivision is partially based on a faulty principle and is, consequently, faulty in a number of cases, the errors are readily corrected, and the result is a system of stereochemical classification entirely free from self-contradiction.

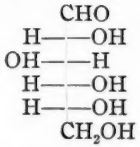
[1] Z. physiol. Chem. **36**, 261 (1902).

[2] See E. O. von Lippmann: "Die Chemie der Zuckerarten," 3d ed. (1904), pp. 366 and 1714.

[3] Z. physiol. Chem. **37**, 221 (1903).

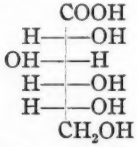
[4] Ibid. **37**, 464 (1903).

But first of all, in the interest of economy of space, I will take the liberty of employing here a stereochemical notation which seems to me more concise and transparent than any hitherto proposed.[1] Ordinary glucose, for instance, whose projection-formula, as simplified by Victor Meyer, is

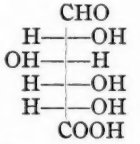


will be represented by the symbol

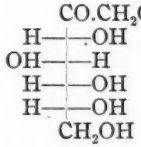
and the same symbol will stand for all other compounds with different terminal groups and stereochemically similar to glucose, such as



δ-Gluconic acid.



δ-Glucuronic acid.



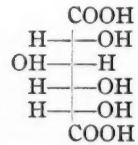
A keto-heptose.

etc.

Similarly, compounds like fructose, arabinose, etc., will be represented by the symbol

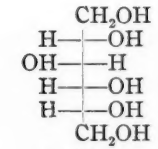
On the other hand, symbols like

for



Saccharic acid.

or



Sorbite.

[1] Compare Lespieau and Maquenne's notation; Lespieau: Bull. soc. chim. [3] 13, 105 (1895), and L. Maquenne: Les Sucres et leurs principaux dérivés, Paris, 1900.

will represent compounds whose molecules consist of two chemically similar halves.

Fischer blends the assignment of each compound to the $\delta$- or the $\lambda$-family with the assignment of a single stereochemical formula to the compound. Thus, after on the one hand choosing the formula

to represent the dextro-rotatory saccharic acid and choosing this acid for founding the $\delta$-family, and after, on the other hand, showing that corresponding to the two glucoses and the two guloses are the two pairs of enantiomorphous formulas:

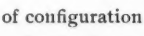
he concludes that the glucose yielding that saccharic acid and the gulose derived from the same acid should be represented, respectively, by formulas I and III *and belong to the same stereochemical family*, viz., the $\delta$-family.

In the latter part of Fischer's conclusion is the fundamental error. While the assignment of formulas is entirely correct, that latter part of the conclusion is based on an assumption that may be formulated as follows: Two aldoses can produce the same dibasic acid only if they belong to the same stereochemical family. That this, however, is erroneous as a general proposition, may be readily seen from the fact that the two enantiomorphous galactoses—plainly belonging to the opposite families—yield the same mucic acid. Similar cases are presented by the pairs of enantiomorphous aldoses yielding allomucic, xylotrioxyglutaric, ribotrioxyglutaric, and mesotartaric acids. True, all these acids are optically inactive by intramolecular compensation. But their example is sufficient warning that *the testimony of a symmetrically constituted compound, whether active or inactive, cannot be relied upon to prove the stereochemical family-relationship of two compounds with dissimilar end-groups.*

Fischer's simultaneous assignment of single formula to aldose and of aldose to family are based mainly on the following forms of relationship: 1, genetic relationship, as just seen, of two sugars

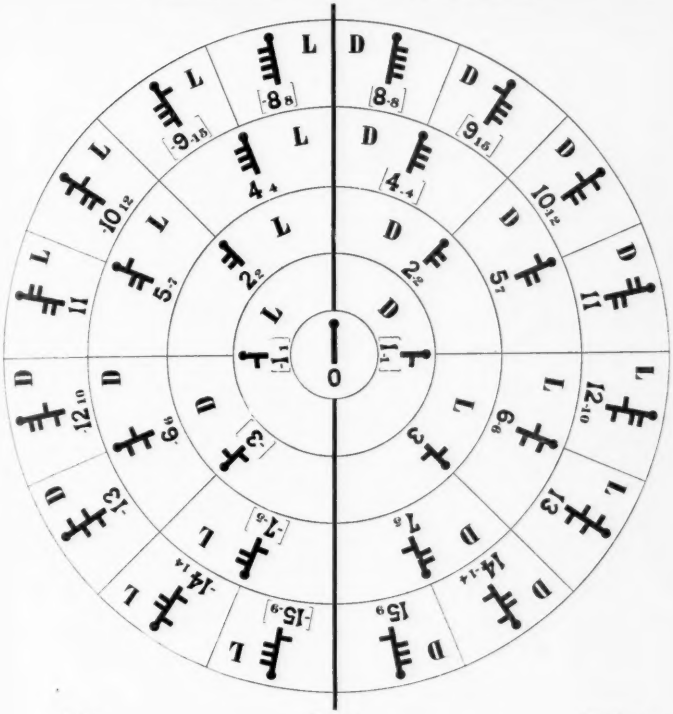
to the same dicarboxylic acid; 2, transformation of two sugars into the same osazone; 3, mutual transmutability of two sugars through their corresponding aldonic acids; 4, transformation of a sugar with $n$ into one with $n+1$ asymmetric carbon atoms by Kiliani's method; 5, transformation of a sugar with $n$ into one with $n-1$ asymmetric carbon atoms by Wohl's method (or the more recent method of Ruff). Now, accepting Fischer's assignment of formulas, and discarding, for the reason just stated, the first of these relationships, the formulas themselves (and hence the sugars labeled by them) may be grouped into two enantiomorphous families as shown in the accompanying table, which embodies practically all the known chemical relationships. Couples of aldoses like 10 and 11, 4 and 5, 2 and 3, are obviously $\alpha$-isomeric: the members of each couple are mutually transformable through their aldonic acids, yield the same osazones, are derived from the same simpler aldoses (*e. g.*, 10 and 11 from 5) by the cyanhydrin reaction, yield the same simpler aldoses by Wohl's or Ruff's method, yield the same ketoses, etc.

The table represents, not the monosaccharides alone, but, in general, any system of stereochemical molecules (with dissimilar halves) uniformly built up from a pair of enantiomorphous molecules with single asymmetric carbon atoms.[1] It must, however, be observed that the same arrangement would result if instead of starting from the simplest pair of enantiomorphous

[1] The formulas to the right of the dividing line (the δ-family) all have the hydroxyl of the basal asymmetric carbon atom turned to the right. This is in accordance with the fact that if the corresponding compounds were all actually built up by Kiliani's method from δ-glycerose, , the HCOH group of the latter would go to form part of the more complex molecules without suffering a change of configuration:  and , etc. In the λ-family the hydroxyl in question is of course invariably turned to the left.

Every sugar marked in the table by an even number (2, 4, —6, etc.) must yield the same dibasic acid and the same alcohol as one of the sugars of the opposite family, because in all even-numbered sugars the hydroxyls of the first and last asymmetric carbon atoms are turned in the same direction. This may be illustrated by an instance. The acid is derivable from the sugars =  and  (—14 and 14), but these sugars belong to the opposite families, as shown by their basal hydroxyls being turned in the opposite directions.

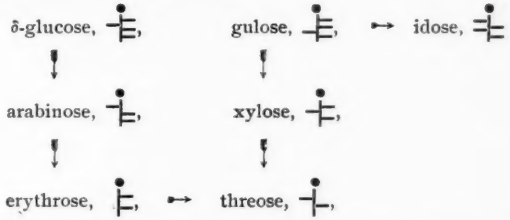
CLASSIFICATION OF STEREOISOMERS.




| Acids. | | Sugars. | | Alcohols. | |
|---|---|---|---|---|---|
| 0. | Oxalic. | 0. | Glycolose; dioxyacetone. | 0. | Ethyleneglycol. |
| 1,–1. | Tartronic. | 1. | Glycerose; erythrulose. | 1,–1. | Glycerol. |
| 2,–2. | Mesotartaric. | 2. | Erythrose; araboketose. | 2,–2. | Mesoerythrite. |
| 3. | Tartaric. | 3. | Threose; xyloketose. | 3. | Erythrite. |
| 4,–4. | Ribotrioxyglutaric. | 4. | Ribose. | 4,–4. | Adonite |
| 5,7. | Trioxyglutaric. | 5. | Arabinose; fructose. | 5,7. | Arabite. |
| 6,–6. | Xylotrioxyglutaric. | 6. | Xylose; sorbinose. | 6,–6. | Xylite. |
| 7,5. | =5,7. | 7. | Lyxose; tagatose. | 7,5. | =5,7. |
| 8,–8. | Allomucic | 8. | Allose. | 8,–8. | .... |
| 9,15. | Talomucic. | 9. | ? | 9,15. | Talite |
| 10,–12. | +Saccharic. | 10. | Glucose. | 10,–12. | —Sorbite. |
| 11. | Mannosaccharic. | 11. | Mannose | 11. | Mannite. |
| 12,–10. | —Saccharic. | 12. | Gulose. | 12,–10. | +Sorbite. |
| 13. | Idosaccharic. | 13. | Idose. | 13. | Idite. |
| 14,–14. | Mucic. | 14 | Galactose. | 14,–14. | Dulcite. |
| 15,9. | =9,15. | 15. | Talose. | 15,9. | =9,15. |

compounds we started from two enantiomorphous pairs of $\alpha$-isomeric compounds with two asymmetric carbon atoms (2,3 and —2, —3). In other words, the fact that the glyceroses have not yet been isolated and correlated with the more complex sugars cannot affect the classification: the known aldotetroses lead to the same result.

The *D*'s and *L*'s in the table exhibit Fischer's classification, and it is seen at a glance that the principle whose unreliability was pointed out above has led to error in the case of the guloses, their $\alpha$-isomeric idoses, their kindred xyloses and threoses[1] (12, —12, 13, —13, 6, —6, and 3, —3, respectively), and all the corresponding aldonic acids, as well as in the case of the sorbinoses (6, —6), the xyloketoses (3, —3), and other derivatives of unsymmetric structure. Thus natural xylose, whose designation as a $\lambda$-compound would mark it as a relative of $\lambda$-glucose, is really a $\delta$-compound, *i. e.*, a relative of natural $\delta$-glucose; and the same is true of its kindred gulose, idose, threose, etc. The set of relationships in question are as follows:




Conversely, the antipodal xylose, gulose, idose, threose, etc., are seen to be really relatives of the artificial $\lambda$-glucose. Plainly, a change in the designation of all such compounds will definitely eliminate a number of current misapprehensions, which partially defeat the very object of the classification. At all events, the transformation effected by Salkowski and Neuberg, important as it certainly is from a physiological point of view, does not by any means constitute a transformation of a $\delta$-compound into a $\lambda$-compound, although it does point clearly to a biochemical relationship between $\delta$-galactose and $\lambda$-arabinose.

The numbers marking the formulas in the table[2] indicate the derivation of dicarboxylic acids and polyatomic alcohols from

[1] Ruff (with Kohn): Ber. **34**, 1370 (1901).

[2] Brackets mark *aldoses* that have not yet been isolated.

the aldoses. Thus aldose 11 ($\delta$-mannose) leads to an acid and an alcohol not derivable from any other aldose. The designation $5_7$ shows that two different aldoses, 5 and 7, the lyxose and arabinose of the same $\delta$-family, yield the same (active) acid and alcohol. The designation $14_{-14}$ shows that the two enantiomorphous galactoses, 14 and —14, yield the same (hence optically inactive) acid and alcohol. Finally, the designation $10_{-12}$ indicates that two aldoses belonging to the opposite families yield the same saccharic acid and sorbite; the aldoses not being enantiomorphous, the acid and alcohol must obviously be optically active. The antipodal acid and alcohol are derived from the aldoses —12 and 10, as indicated by the designation $-12_{10}$. How are such optically active compounds of mixed genealogy—say, ordinary dextro-rotatory saccharic acid—to be designated?[1] The combined symbol $\delta$-$\lambda$ might be misleading, since the symbol *d*-*l* has frequently been used in connection with racemic mixtures. The best way would probably be to denote the sense of the rotatory power by the signs + and — and to remind that the compounds belong to either of the families by the prefix *amphi*. Thus we would have +amphi-saccharic acid and —amphi-saccharic acid, —amphi-sorbite and +amphi-sorbite. A glance at the table shows that the cases in question are *the only ones* in which an active acid and alcohol are derived from two non-enantiomorphous sugars of opposite families. It is easy to foresee, however, that a number of similar cases will be encountered among the monosaccharides with more than four asymmetric carbon atoms.

An important point to note in connection with our subject is that the rectification of the genealogy of the threoses leads directly to a similar rectification in the case of the active tartaric acids, in view of the immediate derivation of these, as well as of the active erythrites, from the threoses.[2] Ordinary tartaric acid,

which is generally believed to be a relative of ordinary $\delta$-glucose, really belongs to the family of $\lambda$-glucose and should be designated $\lambda$-tartaric acid. The direct oxidation which produces ordinary

[1] An independent classification of compounds of symmetrical structure is impossible.

[2] Ruff: Ber. **32**, 3677 (1899); Maquenne and Bertrand: C. R. 132, 149 (1901).

tartaric acid from $\delta$-glucose is scarcely a more reliable criterion than would be a process of destructive distillation. In the same family with 10, *i. e.*, $\delta$-glucose, are the acids of $2_{-2}$ and 3, *i. e.*, mesotartaric and levo-rotatory tartaric acids, and it is the latter, therefore, that should be designated $\delta$-tartaric acid. Similar changes are obviously required in the case of the active erythrites.

Neuberg and Silbermann have recently[1] transformed, by simple reactions, the aldehyde-glyceric acid, $CHO.CHOH.CO_2H$, produced by the action of caustic soda on nitrocellulose,[2] on the one hand into a mixture of levo-rotatory tartaric and mesotartaric acids, on the other hand into levo-rotatory glyceric acid. Levo-rotatory tartaric acid being, according to Fischer, tartaric acid, Neuberg and Silbermann now designate its other relative, levo-rotatory glyceric acid, among the $\lambda$-compounds. "Attention," say the authors, "may especially be called to the *peculiar* circumstance that starting from cellulose, indisputably a derivative of *d*-glucose, one thus passes, by way of nitrocellulose, aldehyde-glyceric acid, and *l*-glyceric acid, from the *d*-family of the carbohydrates into the *l*-family." From what has been said above it is plain that levo-rotatory glyceric acid, being a relative of levo-rotatory tartaric acid, belongs within the same stereochemical family as $\delta$-glucose (and, presumably, cellulose), and should be designated $\delta$-glyceric acid, so that the series of changes in question are neither a transformation of $\delta$-compounds into $\lambda$-compounds, nor in any way "peculiar." The aldehyde-glyceric (glyceruronic ?) acid, too, must be considered as a member of the $\delta$-family, and the same applies to the natural malic and aspartic acids and asparagine, in view of their well-known relationship to levo-rotatory tartaric acid.

I cannot conclude without cordially thanking Professor Morris Loeb, the head of this department, for much valuable help in connection with the present paper.

[1] Z. physiol. Chem. **44**, 134 (1905).

[2] Will: Ber. **24**, 400 (1891).

# PRELIMINARY ANNOUNCEMENT CONCERNING A NEW MERCURY MINERAL FROM TERLINGUA, TEXAS.

By W. F. Hillebrand.

Received December 15, 1905.

The mercury minerals of the Terlingua District, Texas, are noted for the unusual composition of several of their number. Besides cinnabar, calomel, and mercuric oxide, two oxychlorides, eglestonite and terlinguaite, have been described in detail by Prof. A. J. Moses,[1] and a third, as yet unnamed, has been provisionally identified by him as likewise an oxychloride. This last, the No. 5 of Prof. Moses, seems to be the chief mineral on a number of specimens from the Terlingua District lately received for identification from Mr. H. W. Turner. Its examination reveals a composition most singular and apparently representative of a class of compounds hitherto unknown in nature, *viz.*, mercur-ammonium salts. So far as yet known, the qualitative composition is represented by the components Hg, N, Cl, $SO_4$, probably O and possibly H. The tests, both qualitative and quantitative, thus far made, seem to show with little room for doubt that the mercury and nitrogen form the mercur-ammonium radical. Dr. P. G. Nutting, of the Bureau of Standards, has kindly examined spectroscopically the products of progressive heating of the mineral under reduced pressure; and besides nitrogen, mercury, chlorine and sulphur, obtained a small amount of helium. Singularly enough, this last seemed to come off wholly during the first warming of the mineral and before it underwent any visible breaking-up.

The complete examination of this novel mineral and its associated mercury compounds will probably consume much time. In order to reserve the field for the chemical examination by myself and the crystallographical (now in progress) by Mr. W. T. Schaller, this preliminary announcement is made.

U. S. Geological Survey, Washington, D. C.,
December 14, 1905.

[1] Am. J. Sci. **166**, 253 (1903).

## NEW BOOKS.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN. New York: John Wiley & Sons. Price, $3.00.

The third edition of this excellent work has been enlarged from 362 to 522 pages, brought to date, and revised with a view to making its subject appeal to the student as being a tool with which he may obtain results useful for other than simply theoretical purposes.

The revision of the text seems satisfactory: a rapid survey detected no more serious omission than the leaving of the mixture of alcohol and water in a class from which the experiments of W. A. Noyes removed it in 1901. The unnumbered equations on page 6 are true only in one case, which is not specified. Some of the problems on the less recent subjects need further revision. In problem 15, after a question as to the partial pressures in a mixture of gases, we read, "Ans. H = 1.164, O = 1.164, and N = 0.774;" and can only say with the humorist, "this is 2 mutch." The signs of equality involve absurdities, and the use of symbols of the elements as abbreviations of their names is quite out of keeping with the scholarly dignity of the text. In a few cases like this, denominate numbers are printed as abstract numbers. After problem 16, asking the specific gas constant of nitrogen, we read, "Ans. 3007 gr. cm." for 3007 grams per sq. cm. In problem 17, the atomic weight of nitrogen is given as 14.073 and that of hydrogen as 1.032; the answer given is actually that computed from these numbers.

The book is a well rounded and balanced presentation of its subject, and may be heartily commended, either for use in the class-room, or for reading without the aid of a teacher.

EDWARD W. MORLEY.

THE ELECTROLYTIC DISSOCIATION THEORY WITH SOME OF ITS APPLICATIONS. AN ELEMENTARY TREATISE FOR THE USE OF STUDENTS OF CHEMISTRY. By HENRY P. TALBOT, PH.D., Professor of Inorganic and Analytical Chemistry, and ARTHUR A. BLANCHARD, PH.D., Instructor in Inorganic Chemistry at the Massachusetts Institute of Technology. New York: The Macmillan Co. 1905. 82 pp. Price, $1.25 net.

This little volume comes quite opportunely to fill a real want which has been felt by a number of those who have to present

the first- and second-year chemistry in our universities and technical colleges. In it an attempt is made to bring together in concise form the more important of the general principles which underlie the detailed laboratory work of the student during this period, together with enough illustrative examples to bring the theory home to him in his daily work.

As the authors point out in the preface, they have often had to decide between simplicity of statement on one side and accuracy, or at least completeness, on the other. As to just where this line should be drawn is naturally a question which will find almost as many answers as there are teachers of the given field. With this in mind the authors have evidently held the idea of simplicity and brevity uppermost, leaving those who prefer a more rigorous limitation of the general statements of the science to amplify the text in the lectures and discussions which should accompany such a course, thus making the book more flexible as regards its adaptation to existing conditions. This is certainly to be commended, the wide-awake teacher always preferring to amplify rather than expurgate. The book is divided into the following chapters: I. Evidences of Electrolytic Dissociation Afforded by a Study of the Properties of Solutions (20 pages); II. The Law of Mass Action and the Chemical Behavior of Electrolytes (25 pages); III. Electrolytic Solution Pressure (5 pages); IV. Oxidation and Reduction (6 pages); V. The More Common Ions and Their Characteristics (14 pages); VI. Experiments Illustrative of the Theory of Electrolytic Dissociation and Some of its Applications (9 pages).

The treatment throughout is from the kinetic and mechanistic standpoint, the general laws of energetics being left for a later period. Chapter I takes up briefly freezing-point depression, conductivity, osmotic pressure, migration phenomena and chemical activity. Chapter II brings out the importance of solubility, volatility, and ionization with regard to reversible reactions, making free use of the conception of solubility product. The relations of strong and weak acids and bases, hydrolysis and effect of a common ion are then discussed. In Chapter III the solution pressure of both metals and non-metals is dealt with. Chapters IV and V are mainly devoted to expression of the familiar ideas of qualitative analysis in the language of the dissociation theory, including the writing of ion equations. Chapter

VI contains sixteen simple experiments requiring a minimum of special apparatus to illustrate the foregoing text, together with appended questions intended to set the student thinking.

One adverse comment which the reviewer has to make is on the treatment of the semi-permeable membrane which the authors compare (pp. 7 and 8) with a fish net, distinctly committing themselves to the idea of large molecules of solute and small molecules of solvent. This can hardly be accepted as up-to-date even for elementary work. Experience shows that the conceptions of the "membrane" as an intermediate layer of substance in which the "solvent" is itself moderately soluble but the "solute" is practically insoluble is easily grasped by the student, and gives him a far more useful analogy for the purposes of chemical instruction.

The work as a whole is well done, being clearly expressed and up-to-date and deserves a hearty welcome from the teaching force concerned. F. G. COTTRELL.

ANNUAL REPORTS OF THE PROGRESS OF CHEMISTRY FOR 1904. Issued by the Chemical Society. Vol. I. London: Gurney and Jackson. New York: D. Van Nostrand Co. 1905. 280 pp. Price, $2.00 net.

This is the first of a series of reports which are to be prepared and published each year under the auspices of the Chemical Society of London. The subjects treated in the present volume, together with the names of the reviewers, who will be seen to be men well-known in their respective departments, are as follows: General and Physical Chemistry, by James Walker; Inorganic Chemistry, by P. Phillips Bedson; Organic Chemistry—Aliphatic Division, by H. J. H. Fenton; Organic Chemistry—Aromatic and Other Cyclic Divisions, by Julius B. Cohen; Stereochemistry, by William Jackson Pope; Analytical Chemistry, by Alfred Chaston Chapman; Physiological Chemistry, by William Dobinson Halliburton; Agricultural Chemistry and Vegetable Physiology, by John Augustus Voelcker; Mineralogical Chemistry, by Arthur Hutchinson; Radioactivity, by Frederick Soddy.

Speaking generally, the progress of the last year is presented in these reports in a far more readable form than is usual in such reviews, which are apt to deteriorate into annotated bibliographies of publications. Special mention should be made of the article on radioactivity, which is not confined to the work

of the preceding year, but which consists of a brief review, covering 36 pages, of the present state of knowledge in this field.

A. A. NOYES.

METHODS OF ORGANIC ANALYSIS. By HENRY C. SHERMAN, PH.D., Adjunct Professor of Analytical Chemistry in Columbia University. New York: The Macmillan Co. 1905. 8vo. xii + 245 pp. Cloth. Price, $1.75.

"The purpose of this work is to give a connected introductory training in organic analysis, especially as applied to plant and animal substances and their manufactured products." "The descriptions of the methods were written primarily for the use of third-year students in the School of Chemistry, Columbia University, and therefore presupposed a knowledge of inorganic quantitative analysis, elementary organic chemistry and general physics."

The subjects treated are, sampling and the methods for determining nitrogen, sulphur and phosphorus in organic compounds; alcohols, including glycerol, aldehydes and acids. These are followed by chapters upon the carbohydrates, oils, fats and waxes, soaps and lubricants, proteids and cereals, butter, and milk.

A feature of the book that commends itself, is a general presentation of the subject in one chapter, that on carbohydrates for example, followed by a chapter upon the special methods of analysis. Where it is impracticable to give all the methods for the analysis of the various compounds considered, references are made to standard works upon the subject; these are often supplemented by copious foot-notes, making the book encyclopaedic in scope.

While the work makes no pretense of covering the whole field of organic analysis, the subjects treated are well chosen and carefully and fully considered, and it deserves a place beside the treatises of Lunge and Allen.

A. H. GILL.

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## RECENT PUBLICATIONS.

A CONTRIBUTION TO THE CHEMISTRY OF THE TELLURATES; A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY, UNIVERSITY OF WISCONSIN, 1905. By Edgar Burton Hutchins. Madison, Wisconsin: University of Wisconsin. 1905. 39–84 pp. 25 cents.

ENGINEERING CHEMISTRY; A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS, FOR THE USE OF STUDENTS, CHEMISTS AND ENGINEERS. By T. Bliss Stillman. Third Edition. Easton, Pa.: Chemical Publishing Co. 1905. 22+597 pp. $4.50.

SEWERAGE AND SEWAGE PURIFICATION. By Moses Nelson Baker. Second Edition, revised and enlarged. New York: D. Van Nostrand Co. 1905. 4+152 pp. 50 cents.

ÜBER DIE OXYDATION DES STICKSTOFFS IN DER HOCHSPANNUNGSFLAMME. By Johs. Brode. Halle: W. Knapp. 1905. 3+63 pp. Marks 2.50.

TRAITÉ DE CHIMIE ANALYTIQUE. TOME I, ANALYSE PAR LA VOIE SECHE OU AU CHALUMEAU. By C. Blas. Paris: Gauthier-Villars. 209 pp. 8 fr. 50.

TEXT-BOOK OF INORGANIC CHEMISTRY. By Arnold F. Holleman. Issued in English in coöperation with Herman C. Cooper. Second English Edition rewritten. New York: J. Wiley & Sons. 1905. 4+487 pp. $2.50.

LEHRBUCH DER CHEMIE. By A. F. Holleman. Fourth Edition. Leipzig: Veit & Co. 1905. 10+490 pp. Marks 10.

PRÜFUNG DER CHEMISCHEN REAGENZIEN AUF REINHEIT. By E. Merck. Berlin: J. Springer. 1905. 4+281 pp. Marks 2.50.

FÄRBEN UND BLEICHEN VON BAUMWOLLE, WOLLE, SEIDE, JUTE, LEINEN, ETC. ZWEITE TEIL, DIE BLEICHEREI, WASCHEREI UND KARBONISATION. By J. Herzfeld. Second Edition. Berlin: M. Krayn. 1905. 16+450 pp. Marks 11.50.

WESTERN MILL AND SMELTER METHODS OF ANALYSIS; A PRACTICAL LABORATORY HANDBOOK FOR THE ASSAYER AND CHEMIST. By Philip H. Argall. Denver, Col.: Industrial Printing and Publishing Co. 1905. 124 pp. $1.50.

PRODUCTION OF CHROMIUM AND ITS COMPOUNDS BY THE AID OF THE ELECTRIC CURRENT. By Max Le Blanc. Authorized English translation by Joseph W. Richards. Easton, Pa.: Chemical Publishing Co. 1904. 122 pp. $1.25.

MANUAL OF CHEMISTRY; INORGANIC AND ORGANIC. By A. P. Luff and F. J. M. Page. Third revised Edition. Chicago: W. T. Keener & Co. 1905. 555 pp. $1.75.

TECHNICAL METHODS OF ORE ANALYSIS. By Albert H. Low. New York: John Wiley & Sons. 1905. 10+273 pp. $3.00.

ANLEITUNG ZUR QUALITATIVEN ANALYSE ANORGANISCHER UND ORGANISCHER STOFFE SOWIE ZUR TOXIKOLOGISCH- UND MEDIZINISCH-CHEMISCHEN ANALYSE. By Carl Arnold. Fifth Edition. Hannover: C. Meyer. 1905. 8+278 pp. Marks 7.

ÜBER DIE BESTIMMUNG DER PHOSPHORSÄURE ALS MAGNESIUM-AMMONIUMPHOSPHAT UND ALS AMMONIUMPHOSPHOMOLYBDAT. By Gunner Jörgensen. Kopenhagen: A. F. Host & Son. 1905. 100 pp. Marks 3.60.

ZUR GESCHICHTE DER ZUCKERFABRIKATION. By G. Fr. Meyer. Braunschweig: Appelhans. 1905. 8+116 pp. Marks 4.

THREE YEARS' COURSE OF PRACTICAL CHEMISTRY. FIRST AND SECOND YEARS. By G. H. Martin. London: Rivingtons. 1905. 1/6.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS, BASED UPON THE APPLICATION OF THE THEORY OF ELECTROLYTIC DISSOCIATION AND THE LAW OF MASS ACTION. By Edgar H. Summerfield Bailey and Hamilton P. Cady. Fifth Edition. Philadelphia: P. Blakiston's Sons & Co. 1905. 10+278 pp. $1.25.

SELECT METHODS IN CHEMICAL ANALYSIS (CHIEFLY INORGANIC). By Sir William Crookes. Fourth Edition. New York: Longmans, Green & Co. 1905. 23+738 pp. $8.00.

THE SPIRIT OF ORGANIC CHEMISTRY; AN INTRODUCTION TO THE CURRENT LITERATURE OF THE SUBJECT. By Arthur Lachman. New Edition. New York: Macmillan. 1905. 18+229 pp. $1.50.

MANUAL OF CHEMISTRY; A GUIDE TO LECTURES AND LABORATORY WORK FOR BEGINNERS IN CHEMISTRY. By W. Simon. Philadelphia: Lea Brothers & Co. 1905. 17+643 pp. $3.00.

SECOND YEAR CHEMISTRY; A HANDBOOK FOR LABORATORY AND CLASS WORK. By E. Hart. Easton, Pa.: Chemical Publishing Co. 1905. 6+165 pp. $1.25.

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